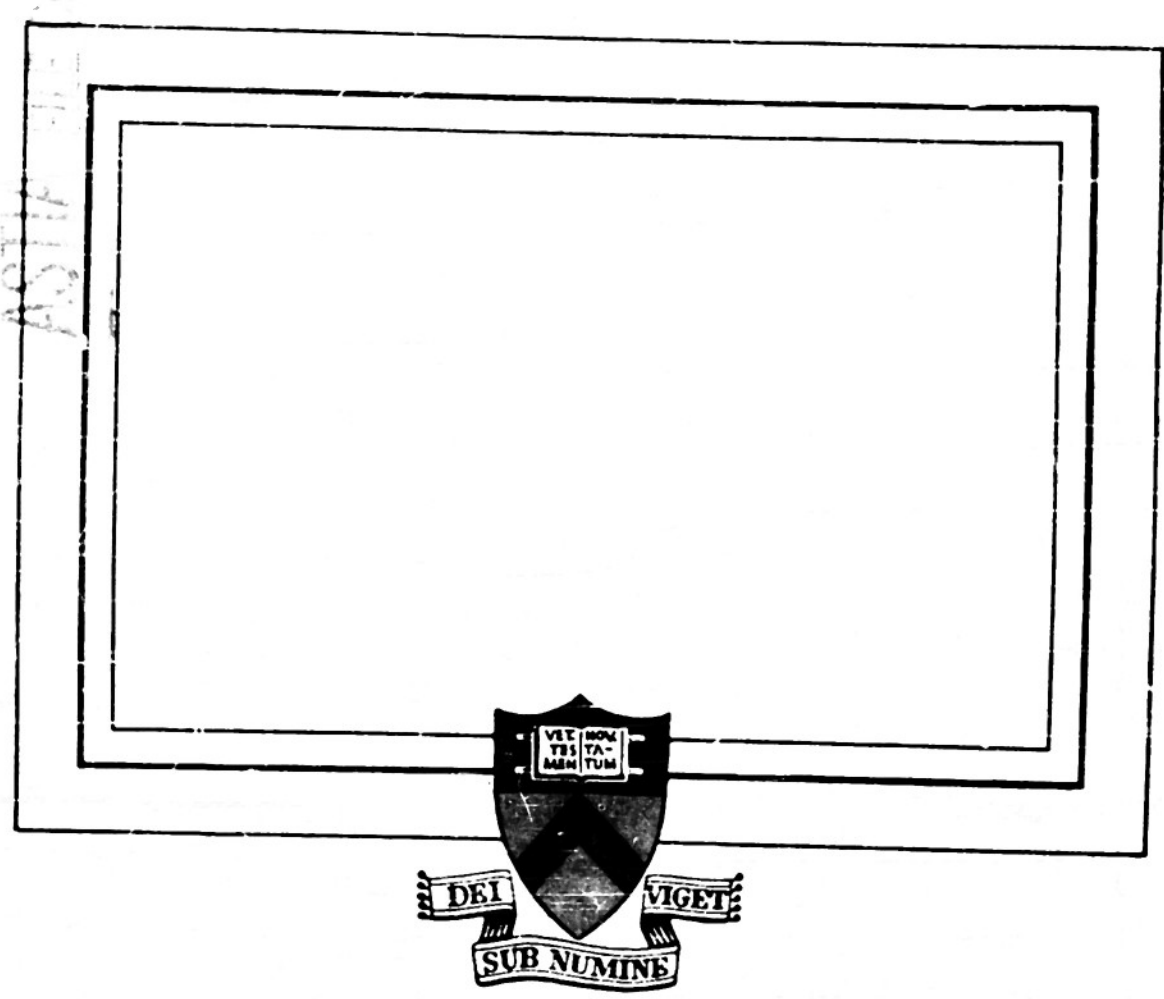


UNCLASSIFIED

AD NUMBER	
AD019271	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	confidential
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 01 JUL 1953. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203.	
AUTHORITY	
31 Jul 1965, DoDD 5200.10; ONR ltr, 26 Oct 1977	

THIS PAGE IS UNCLASSIFIED

11-2-61
AD No 19271



PRINCETON UNIVERSITY

CONFIDENTIAL
Security Information

CONFIDENTIAL
Security Information

Final Report For
Project 092-064, Task order N6onr-27017
Covering the period July 1st, 1950, to July 1st, 1953.

Submitted by G. C. Akerlof

Forrestal Research Center

Princeton University

1. Purpose of study

At present there are two processes in use for the production of hydrazine, the Raschig ammonia and the urea hypochlorite method with either caustic dehydration or ammonolysis to get an anhydrous product. As potential processes may be listed the oxidation of ammonia by air, nitrous oxide or chlorine, the decomposition of bisnitroso-iso-butylene chloride and electric discharge processes. It was the purpose of the study made to find out if the formation of hydrazine from ammonia in a glow discharge could be utilized for its production on a large scale. Among the more important factors to be considered were yield of hydrazine per KWH, degree of ammonia decomposition, and conversion per pass and sufficient reactor size.

June 1953

CONFIDENTIAL
Security Information

CONFIDENTIAL

Security Information

ABSTRACT

A short review is given of work performed under the contract from its inception to its finish. As final conclusion it is recommended that:

- 1) an engineering study of collected data be made;
- 2) proposed designs for large reactors be critically reviewed;
- 3) some measurements be made with ammonia flows in the range 2-6 CFM or higher under flow conditions adjusted to give high yield and high degree of conversion;
- 4) a limited study be made of yield and conversion obtainable with electrodeless discharges using reactors with dielectrics having high dielectric constants.

CONFIDENTIAL

Security Information

CONFIDENTIAL

Security Information

2. Review of work completed during the first year at the Mellon Institute in Pittsburgh

Introduction At the time the study of the formation of hydrazine was started we worked entirely with relatively small ammonia flows, small reactors and low power inputs. Towards the end of the first year we began to increase the general level of the ammonia flow rate, the size of the reactors and the power consumption in the discharge. The limit of the capacities of our flow systems and power supply was soon reached and the difficult problem of the design of reactors that could be enlarged in size more or less at will, which would be a prerequisite for a worthwhile process, had to be deferred to the future.

Experimental methods and types of reactors used A short summary should be sufficient. The simplest method of handling ammonia flows of a few up to about a hundred liters per minute with the vacuum pumps available at the time consisted of complete absorption of the ammonia in sulfuric acid of suitable concentration. The apparatus built for the purpose allowed taking a large number of samples over an extended period of time. The amount of hydrazine present in each sample was determined iodometrically using the method of Audrieth. A continuous hydrazine analyzer utilizing the heat developed when hydrazine vapor contacts a palladium catalyst was built, but it was found to be unstable and sufficient time to study its behavior in detail was not available.

The main DC power supply employed was an RA-38 full wave rectifier which gave a carefully filtered, smooth, high voltage current. A generator for the production of pulsed, high voltage DC current was developed.

CONFIDENTIAL

Security Information

CONFIDENTIAL

Security Information

The amplitude, width and repetition rate of the pulse were controllable thereby offering as much flexibility as possible within reasonable limits. As source of high voltage 60 cycle AC either an X-ray or a tapped single phase 7.5 KVA transformer was employed. The different types of reactors built and tried out may be listed as follows:

1. Magnetically dispersed discharges between stationary or rotating electrodes of different forms with the magnetic field at right angle to the discharge and the ammonia flow taking place
 - a) at right angle to the longer axis of the cross section of the field giving a short path and contact time.
 - b) parallel to the longer axis of the cross section of the field giving a relatively long path and contact time.
 - c) in the direction of the field as accomplished by using a porous plate and giving a short path in the discharge.
2. Discharge between stationary point electrodes with the gas admitted and leaving the discharge chamber through long narrow slits.
3. Discharge between perforated large plane electrodes through a thin porous plate inserted between them.
4. Discharge between a large number of sharp points and a plane continuous metal surface or a wire net.
5. Discharge between stationary point electrodes through long, narrow water-cooled glass tubes.
 - a) using smooth bore tubes. Employed for all kinetic studies
 - b) with helically fluted tubes and other forms
 - c) with addition of solvent spray
6. Discharge in microwave cavities at wave lengths of 1.25 and 3.20 cm.
7. Discharge between stationary ring electrodes in a conical cyclone.

CONFIDENTIAL

Security Information

CONFIDENTIAL

Security Information

Measurements were made with all these different types of reactors except the last one. The microwave cavity cell with a wave length of 1.25 cm. did not produce any hydrazine, but in all other cases some yield was found. The all glass reactors were simplest and cheapest to make and could evidently also be fashioned as the most efficient ones.

Experimental results A few experiments established very soon that the yield of hydrazine per KWH obtainable with 60 cycle AC glow discharges were considerably lower than those measured with either straight or pulsed DC which latter were both of the same order of magnitude. The yield obtained per KWH did not vary with considerable changes in the temperature of the reacting system. The reactor was placed inside a large cold box, the temperature of which could be controlled accurately down to -40°C . The cooling liquid for the reactor was circulated at a high rate through relatively large finned refrigerator type heat exchangers.

To study the rate of formation and decomposition of hydrazine in an electric discharge the following reactions were assumed to take place:



It was further assumed that A) all three reactions were monomolecular in nature and B) reaction 2) is very fast when compared with reaction 1). Since the rate of decomposition K_2 of hydrazine was very much larger than its rate of formation we could, without making an appreciable error, use the following equation for its computation:

CONFIDENTIAL

Security Information

$$y_1/y_2 = (1 - e^{-k_2 t_1}) / (1 - e^{-k_2 t_2})$$

where y_1 and y_2 represent the hydrazine yield obtained at times t_1 and t_2 respectively. Introducing the value of k_2 found by successive approximation in the expression for y_1 :

$$y_1 = \frac{a k_1}{k_2 - k_1} \cdot (e^{-k_1 t} - e^{-k_2 t})$$

where a is the initial ammonia concentration and k_1 the rate of formation of hydrazine; the value of the latter could also be computed.

The experimental data required were obtained with a tapped glass reactor like the one shown in Fig. 1. The gas samples were withdrawn from the reactor tube at the evenly spaced outlet points and condensed in liquid air. Table I. gives a summary of some data obtained with this tapped reactor. As illustrated in Fig. 2, the rate of formation increases rapidly with the power input or the ammonia flow rate, indicating best power yields are obtained at highest space velocities. Fig. 3 shows the variation of both the rates of formation and decomposition and the change of their ratio with the power input. The most striking result obtained is undoubtedly that rates of formation and decomposition follow each other fairly well and give a ratio that, like the amount of ammonia converted into hydrazine, is practically independent of the power input. However, as the latter increases the amount of ammonia decomposed also increases while the yield of hydrazine per KWH rapidly decreases.

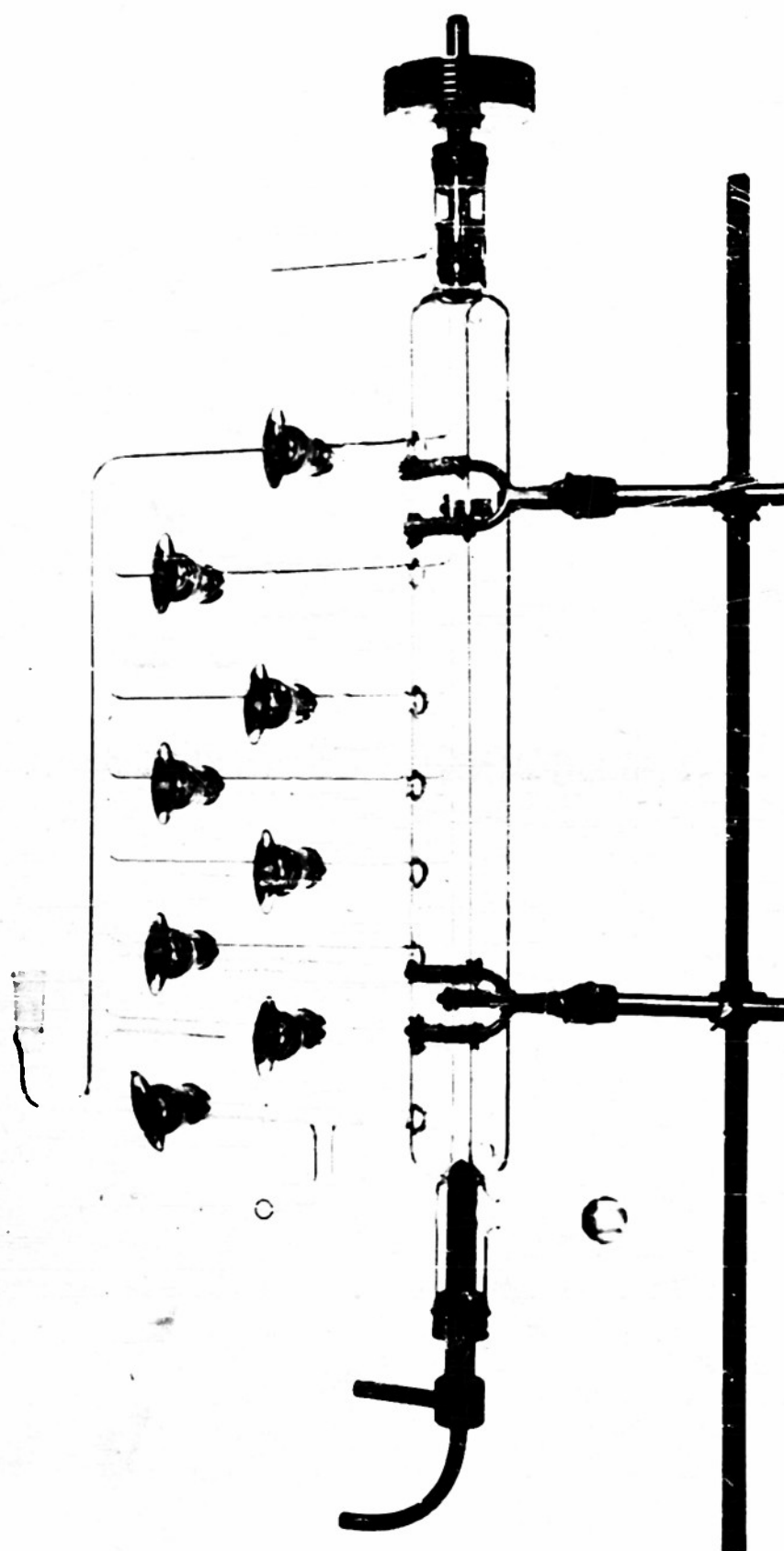


Figure 1

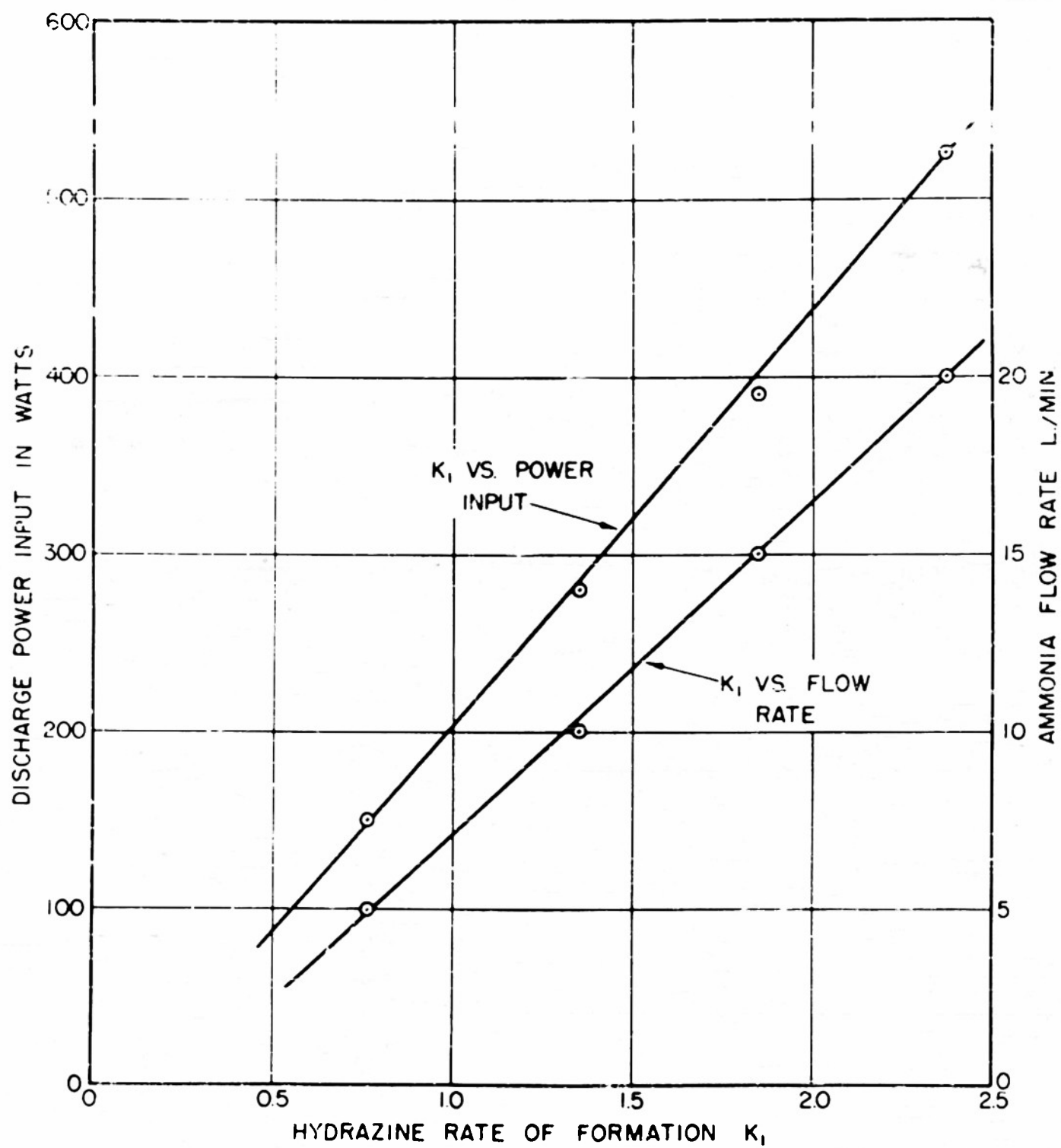


Figure 2

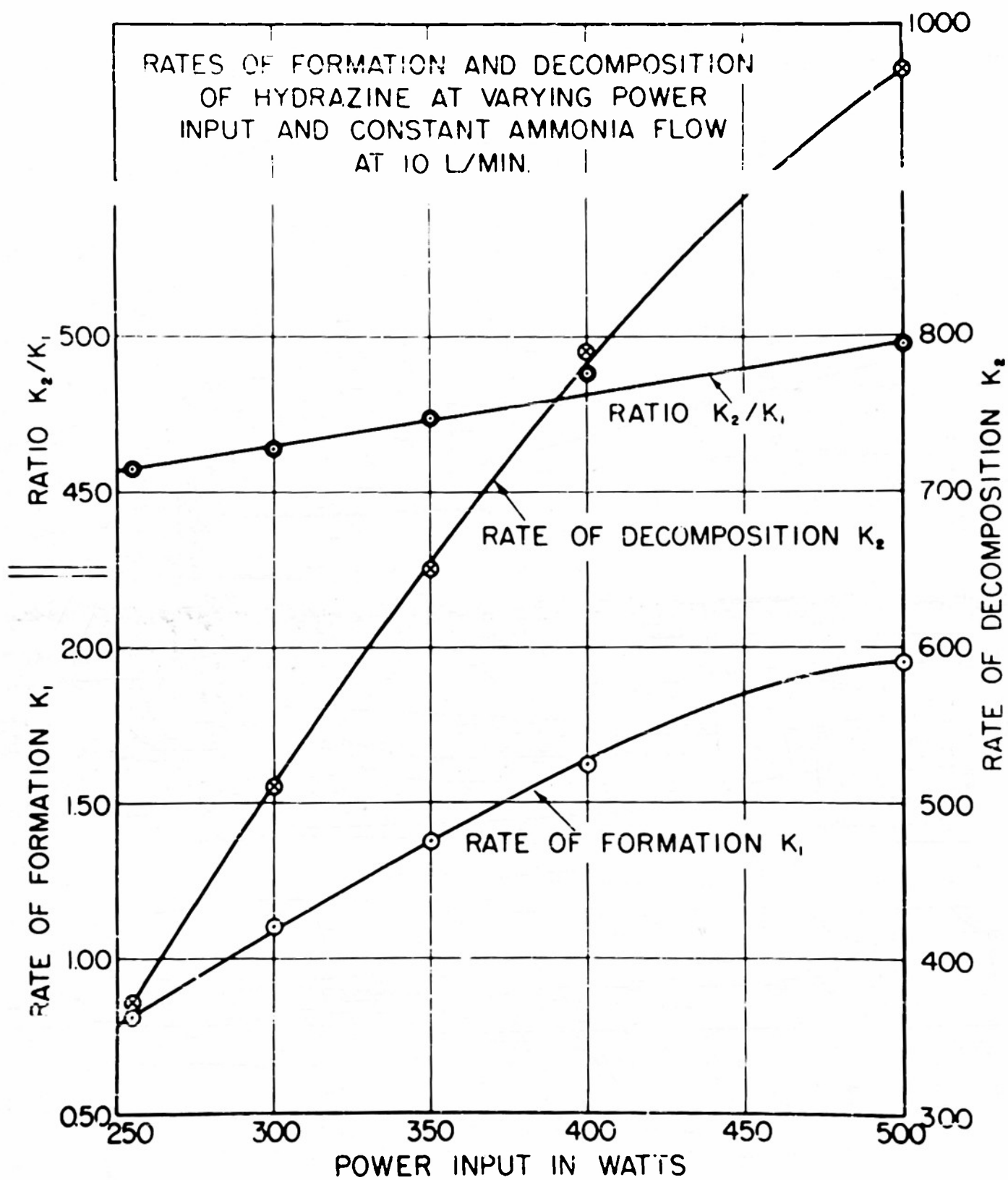


Table I. Hydrazine Yields in Mols/cc $\times 10^{10}$ as Obtained with a DC Discharge in a Tapped Reactor of 8 mm ID at Different Ammonia Flow Velocities

Point	Distance from cathode (inches)	5 lit./min.		10 lit./min.	
		Time millisec.	H ₄ N ₂ yield	Time millisec.	H ₄ N ₂ yield
1	4	1.61	8.3	0.81	9.9
2	7	2.82	10.9	1.41	12.8
3	10	4.02	12.4	2.01	14.4
4	12	4.84	12.5	2.42	15.9
5	14	5.64	12.8	2.82	16.9
6	16	6.44	13.8	3.22	17.7
7	18	7.24	14.6	3.62	18.7
8	20	8.04	(18.1)	4.02	(23.2)
		15 lit./min		20 lit./min	
1	4	0.54	10.7	0.40	9.9
2	7	0.94	13.5	0.70	14.2
3	10	1.34	15.4	1.00	17.6
4	12	1.61	16.4	1.21	19.5
5	14	1.88	18.1	1.41	21.4
6	16	2.15	19.2	1.61	23.7
7	18	2.41	19.4	1.81	26.0
8	20	2.68	(22.6)	2.01	(22.7)

All data were corrected to an average pressure of 24 mm Hg and an average gas temperature of 50°C was assumed.

Table Ia. Values for Yield, Rates of Formation and Decomposition of Hydrazine in a DC Discharge at Different Ammonia Flow Velocities as Computed from the Data in Table I.

Time in millisec.	Hydrazine Yield Moles/cc x 10 ¹⁰			
	5 lit./min.	10 lit./min.	15 lit./min.	20 lit./min.
0.5	-	6.5	3.8	11.3
1.0	6.6	10.7	14.4	18.3
1.5	-	13.3	17.8	22.6
2.0	9.8	15.0	20.1	25.2
3.0	11.5	16.8	22.3	27.8
4.0	12.3	17.4	23.2	28.8
5.0	12.7	17.8	23.5	29.1
6.0	12.9	17.8	23.7	29.2
8.0	12.9	17.8	23.7	29.2
k_1 (formation)	0.76	1.35	1.85	2.37
k_2 (decompn.)	700	900	930	960
Hydrazine yield, gr./KWH	5.2	6.1	6.1	5.0
Power input, watts	150	280	390	535
Current, milliamp.	30	39	43	50
Total conversion, per cent	0.36	0.37	0.35	0.30

The power input for the electric discharge was at all times held close to the minimum sustaining energy required.

Figure 3.

As a general conclusion, to obtain maximum hydrazine yields and least amount of destruction of the ammonia the discharge must be operated as closely as possible at minimum sustaining energy.

In the evaluation of a discharge process for the synthesis of hydrazine the influence of its decomposition products on the yield should be considered. Using a tapped reactor, it was found that when present in small quantities neither hydrogen nor nitrogen had any larger influence on the hydrazine yield. Even the presence of 5% of a highly reactive gas like oxygen did not seem to have any appreciable effect on the yield. Larger quantities of nitrogen and hydrogen apparently acted as diluents only. The data obtained seemed to indicate that the ammonia gas could be passed through a series of reactors before it was necessary to remove the permanent gases formed and provided the hydrazine content is stripped out between each stage. If, let us say, the content of permanent gases in the ammonia increased 0.5% per pass and a total of 5% could be tolerated we would need to liquefy the ammonia and bleed off these gases at every tenth pass only.

A large amount of work was done on hydrazine yield as a function of reactor design. Some measurements with a tapped, tubular reactor having an inner diameter of 10 mm seemed to show that the layers of gas close to the wall were practically undisturbed by the discharge and reacted only to a slight extent. To obtain better contact between the discharge and the entire gas volume a series of reactors having walls with different types of protrusions and cavities but otherwise of identical size were

made up, but none of them gave any distinct advantage over one with smooth walls. However, considerable improvement was obtained when the reactor walls were fluted helically, and hydrazine yields of over 20 grams per KWH were measured with a reactor of this type.

As a result of the work performed during the first year it has been established: 1) hydrazine is produced from ammonia in electric discharges of practically any frequency, 2) the yields may appear to be highest for pure DC current but comparable values were also found at frequencies of a few megacycles, 3) the yield is not affected by considerable variations in operating temperature, 4) the yield is larger the higher the discharge potential and the lower the current, 5) the yield did not seem to be affected by the presence of moderate amounts of neutral gases like N_2 , H_2 , and O_2 , 6) the rate of decomposition of hydrazine in the discharge is about 500 times larger than its rate of formation, limiting sharply the degree of ammonia conversion attainable.

Review of Work Completed at the Naval Powder Factory

As the size of the reactors and the power input increased the disposal of the large quantities of ammonia handled became a decided problem, which was mainly responsible for moving the project. Before work could be started at Indian Head it was, however, necessary to build and test a new high voltage DC power supply and control circuit with sufficient capacity to handle all our foreseeable needs. Also the ammonia flow system had to be increased in size to take care of relatively large flows in the pressure range usually employed.

A considerable number of measurements were carried out with a series of helically fluted, water-cooled tubular reactors of different sizes. As a general conclusion it was found that they were unsuitable as basis for the design of really large reactors. With increasing inner diameter both yield and degree of ammonia conversion dropped off fast. A reactor in which the ammonia flow was guided to follow the contour of a wavy conical cavity was also built, but it failed to stand up under the influence of the electrical field applied and short-circuited incessantly after comparatively short trial runs. The few data obtained seemed to indicate the the degree of ammonia conversion was poor, in agreement with some earlier results that had been collected with a small reactor somewhat similar in principle but built entirely of glass.

Some experiments were made with regard to the effect of a weak- β emitter on the hydrazine yield. After a number of measurements had been carried out as usual with the reactor chosen for the purpose, a short piece of activated palladium wire was inserted close to the geometrical center of the reactor. Then the same measurements as were made before were repeated. Least squaring the series of data obtained at two different flow rates and two different pressures with and without the β -emitter present, it was found as had been anticipated that the latter did not have a measurable influence on the yield of hydrazine obtained.

A preliminary study, with a somewhat different approach, of the effect of radioactive substances on the conversion of ammonia to hydrazine has been made by H.M. Busey (Exploratory Studies of Hydrazine Formation

by Radioactive Ionization, Los Alamos Report LA-1376, June 1951). He found that only the ionization density found in a high flux pile or near concentrated sources was sufficient to produce hydrazine at a practical rate. Thus ionization from waste fission products without preliminary concentration would not be a practical source for hydrazine production. Hydrazine did not in any case seem to form when gaseous ammonia was used. In all cases in which a definite yield of hydrazine was measured liquid ammonia was employed. The best yields were obtained using the beta flux from activated silver. The study of Busey did little more than prove that hydrazine is formed in appreciable quantities when liquid ammonia is exposed to β -radiation. Further study to obtain data under various physical conditions at the high flux densities required would be a major undertaking.

Brief Review of the Literature Pertaining to the Formation of Hydrazine and the Decomposition of Ammonia in Electric Discharges

The formation of hydrazine and the decomposition of ammonia in an electric discharge has been studied quite extensively. Much of this work since 1900 is reviewed below (Ref. 1-66), but no attempt has been made to present a complete coverage of the literature.

A spectral analysis of ammonia and its decomposition products in the electric discharge has been obtained repeatedly (1, 3, 6, 8, 10, 12-17, 19-22, 25, 27-31, 33, 39, 40, 42, 43, 46, 52, 54, 61, 62, 65, 66). Under proper operating conditions the presence of the so-called Schuster bands in the yellow-green portion of the visible spectrum was generally noted in the above work except in one case (ref. 10) or under conditions

where a pulse discharge was employed (65, 66). It has been stated that at sufficiently high discharge currents (1, 8) or at very low flow rates and pressures (3, 42) these bands are extinguished. Their origin is still in doubt; it is known, however, that no Schuster bands are found when $N_2 - H_2$ mixtures are passed through the discharge (42, 66).

Almost all investigators report the presence of N_2 bands but no lines due to N atoms; the bands increase in intensity as the pressure is lowered (10, 52). The presence of H_2 bands or Balmer H lines has been noted (3, 10, 13, 20, 28-31, 42, 46, 52, 65, 66); at lower pressures their intensity diminishes (10, 52) or passes through a maximum (29). The ultraviolet bands attributed to NH have been detected at pressures up to 2 atmospheres (3, 10, 13, 20, 21, 25, 28-31, 42, 43, 46, 52, 65, 66); their intensity also diminishes with decreasing pressures. The presence of the " " bands" in the spectral region 4000-6600 Å is documented in a number of publications (8, 10, 20, 21, 46, 52, 60, 65, 66); these have been associated with the presence of NH_2 radicals. Finally, weak bands originating from the ionic species NH^+ (20) or N_2^+ (10, 20, 29) have been identified.

The formation of ions has also been studied extensively (4, 44, 45, 54, 55, 59), using controlled electron beams in an apparatus of appropriate design or in mass spectrometers. The principal ions formed under these conditions are NH_3^+ , NH_2^+ ; NH^+ , N^+ or N_2^+ are present in somewhat smaller amounts (4, 45, 55). Among the negative ions H^- , Nh^- , and NH_2^- predominate (45, 55) but their concentration is low. All such experiments were

carried out in the pressure range 10^{-3} to 10^{-5} mmHg, and it would be of interest to determine how the ratio of abundance of these ions is altered at the prevailing pressure of the discharge (5 mm Hg and up).

Selected physical characteristics of NH_3 subjected to electron beams or electric discharges have been under study as well. The ionization potential for NH_3 has been variously reported as 11 (62), 10 (59), 10.5 (45), 11.1 (44), and 11.2 (4) electron volts. However, certain ionization processes do occur at values of 6 ± 1 (54), 9 ± 1.4 (56) and 9 (7) e.v. respectively; these are possibly associated with the formation of negative ions as was pointed out clearly in Ref. (7). Other physical characteristics are described in references (2, 8, 35, 36, 62).

Cross sections for all types of electronic collisions with ammonia have been determined (2, 9) and summarized (34). The cross section exhibits a deep minimum near $\bar{V} = 1.5 \text{ volts}^{\frac{1}{2}}$; it rises steeply with decreasing voltages and goes through a maximum with increasing voltages near $\bar{V} = 3 \text{ volts}^{\frac{1}{2}}$. The partial pressure of ammonia in these experiments was in the range 10^{-2} to 10^{-3} mmHg. It is evident that the discharge conditions should be adjusted such that the region of minimum cross section is avoided.

Many authors report (11, 13, 37, 46, 64) that the decomposition of ammonia follows a first order law; however, the rate constant depends on the electrical discharge characteristics as is to be expected in a non-thermal process. The rate of decomposition at first increases

roughly linearly with current; when large currents are applied the rise is more marked. The decomposition also occurs more readily if the temperature of the reaction vessel is allowed to rise (37, 65). Similarly the decomposition rate increases with increasing interelectrode potential.

The relative composition of the nitrogen-hydrogen mixture resulting from ammonia decomposition is very close to the ratio 1:3 (1, 33, 65). Under static conditions an equilibrium between NH_3 , N_2 , and H_2 is reached (11, 37, 64); this state is also reached if N_2 - H_2 mixtures are passed through the discharge (11) but the "equilibrium constant" for these reactions depends on the electrical characteristics of the discharge as well as on the ratio of N_2 to H_2 used in the starting mixture (11). The above kinetic data make it appear as though the discharge decomposition of ammonia occurred via a quasi-thermal unimolecular reaction scheme, with the electronic collisions furnishing the necessary activation energy.

There seems complete agreement among all investigators that in a static system only traces of hydrazine are formed by decomposition of ammonia in a discharge (see esp. ref. (11, 32)). The conversion and power yields for hydrazine formation in a flow system depend very strongly on the conditions employed, and there is some divergence of opinion as to the observed effects. As the flow rate of ammonia is increased under constant electrical conditions the conversion of NH_3 into N_2H_4 is stated to pass through a maximum (8, 33) in a 50 cycle AC glow discharge or to decrease (47). It is evident that since at zero flow no N_2H_4 is formed,

the conversion must first increase to a maximum in order that the Japanese investigators (47) could detect the decrease over the range of flow rates studied by them. The mol or gram percent conversion, which differ by a factor of roughly 2, obtained by different workers are generally in the very low range of 0.02 to 1%. As the power input is increased the conversion was found to decrease somewhat (48).

The power yield of hydrazine was found to increase with (8, 33, 44) or to be roughly independent of (54) flow rate. An increase in gas pressure from 40 to 280 mm drastically lowers the power yield using 50 cycles/sec. or 3 mc/sec. current (1, 8). Increases in power input are found to be detrimental to power yields (8). Power yields in the range 0.3 to 6 g/kWh are reported.

It is well known that hydrazine is thermally unstable; it also decomposes readily when subjected to photon or electrical bombardment. Undoubtedly one of the reasons why high power inputs are detrimental to hydrazine conversion is that under such conditions much of the hydrazine formed is decomposed before it can be extracted from the discharge zone (33). Thus, mild discharge conditions would be expected to favor hydrazine formation, as is found to be the case (8, 32, 33). Also, the use of d.c. pulse discharges, with sufficient time lapse to remove N_2H_4 between the pulses, is found to increase the yield markedly (47, 65).

The admixture of foreign gases affects the ammonia decomposition in the discharge. The presence of traces of moisture is stated to lower power yields by 10 to 30% (38); the admixture of H_2 lowers the rate

of decomposition appreciably (37, 64), while the use of N_2 or O_2 increases this rate (37, 64).

An extensive review concerning the energetics involved in the various processes and reactions which may occur in the discharge has recently been published (1). Some 70 reactions relating to the primary decomposition of ammonia and to the secondary interactions between ammonia, free radical fragments, ions, and hydrazine are discussed. In view of the complexity of the overall reaction scheme, and since spectral and mass spectrometer data reveal the presence of a large number of reacting species, it appears that the process of formation of hydrazine from ammonia in electric discharges is but little understood at this time.

Summary of Results Obtained on Decomposition of Ammonia in Electric Discharges with Bench Scale Apparatus

In a separate report the decomposition of ammonia in an electric discharge, using bench scale apparatus, is described. These results are briefly summarized below.

A water cooled Pyrex glass tube, 0.8 cm diameter, 15 cm in length, served as the reactor. The longitudinal discharge was maintained between two copper electrodes. Ammonia or noncondensable gases were introduced to the reactor through reducing valves and flowmeters. Hydrazine or water vapor could be introduced through capillary leaks if desired. After passing through the discharge tube a portion of the effluent gas mixture was led to an analytical vacuum manifold, which had been previously

evacuated to pressures less than 1 . Upon measuring the gas pressure in the analytical manifold, a five-liter glass bulb was removed to the analytical laboratory for hydrazine assay. Another two-liter bulb was isolated from the analytical manifold and its cold finger immersed in liquid nitrogen to freeze out condensable gases. After a lapse of 30 minutes the pressure of the noncondensable gases was determined. When diluents were employed in this work a blank sample was also obtained in the absence of the discharge to ascertain the composition of the starting mixture.

The hydrazine assay was carried out by absorbing the gas in 0.1 N hydrochloric acid, diluting aliquot portions, and developing color with p-dimethylamino-benzaldehyde. The light absorption was read on an electro-photometer.

The decomposition of pure ammonia into hydrogen and nitrogen can be characterized by the empirical equation

$$x_{nc} = 7.4 \times 10^{-4} W / F - 0.026$$

where x_{nc} is the mole fraction of noncondensable gases in the effluent mixture, W the power input in watts, and F the flow rate in l/min. This equation is obeyed over power inputs ranging from 50 to 675 watts and over flow rates ranging from 1 to 10 l./min. The decomposition of ammonia into its elements is found to be independent of reactor pressure in the range 3 to 50 mm Hg.

Results concerning the decomposition of pure ammonia into hydrazine showed somewhat erratic scattering. It was found that the mol fraction

of hydrazine, $x_{N_2H_4}$, obtained in the product mixture did not depend markedly on pressure or on the ratio W/F in the range $0 < W/F < 160$. In this region all $x_{N_2H_4}$ values were observed experimentally to fall in the range 1.5×10^{-3} to 3.8×10^{-3} . The average $x_{N_2H_4}$ value obtained at a given flow rate increased slightly with decreasing flow rate. For values of $W/F > 160$ the quantity $x_{N_2H_4}$ decreased rapidly. Power yields ranged from 0.04 to 8 g. hydrazine per KWH, the most favorable yields being obtained at the lowest possible power inputs. The conversions obtained were in the range 0.4 to 0.8 g. hydrazine per 100 g. ammonia. For the majority of experimental conditions the ratio of moles of noncondensable gases to hydrazine produced in the discharge was in the range 200-300.

When nitrogen was used as diluent in 50-50 mixtures, the decomposition of ammonia into its elements was decreased by a factor of two, and the decomposition into hydrazine was not affected appreciably. Small quantities of water vapor were found to lower the hydrazine yield by a factor of two. Using hydrogen, the ammonia decomposition into the elements was suppressed but the formation of hydrazine was greatly enhanced. The fraction of ammonia in the starting mixture converted to hydrazine, z , passed through a sharp maximum as the power input was raised. Under optimum conditions z -values in the range of .7 to 1.2 mol percent were found, corresponding to a maximum conversion of 1.2 g hydrazine per 100 g of ammonia. Power yields in this set of experiments were in the range 2.1 to 13 g/KWH. Use of helium in 40:60 ratios enhanced decomposition of ammonia both into the elements and into hydrazine. Again the quantity z was found to pass

through a sharp maximum as the power input was raised. Fractional conversions up to $x = 1.7$ mol percent were reached, corresponding to conversions of 3.4 g hydrazine per 100 g. ammonia introduced into the reactor. Depending on operating conditions, power yields ranging between 0.7 and 22 g/FWH were observed, with highest values being found at the lowest possible power inputs and at flow rates in the range 2.1 to 3.4 l/min. Thus the use of hydrogen or helium as a diluent seems to be favorable to the formation of hydrazine.

The decomposition of hydrazine in the discharge was also investigated, using ammonia, hydrogen, nitrogen and helium as carrier gas. With initial hydrazine concentrations in the range up to 4 mol percent, decomposition was found to occur readily in the discharge, the extent of which increased roughly linearly with power input. After the hydrazine concentration reached a value ranging from one to three tenths of the initial concentration, the rate of further decomposition with increasing power input levelled off.

The Formation of Hydrazine from Ammonia in Glow or Electrodeless Discharges as a Method of Large-Scale Production

The Parsons report (Hydrazine Study for Navy Department, Bureau of Aeronautics, October 1950; R.M. Parsons Company, Los Angeles, Cal.) analyzed the cost of large-scale production of hydrazine using a number of different processes. The cost data for the individual processes finally arrived at were later challenged, particularly the values computed for the only practical processes in use at the present time. The formation of hydrazine from

ammonia in a glow discharge was treated as a potential process with the estimated cost of production based on experimental data available at the time. Reforming costs for the ammonia decomposed would undoubtedly be higher than was assumed at the time and the same would seem to be true for power (0.5 cent/KWH) and ammonia (\$32 per ton as against present day price of \$32/ton). Finally, although much higher yields of hydrazine per KWH power input in the discharge than the value adopted at the time may be obtained, the degree of ammonia conversion would be correspondingly lower, rapidly increasing the cost of isolation of the hydrazine formed. Even though the cost of large-scale production of hydrazine employing the practical processes now in use as estimated by Parsons may have to be more than doubled, the cost if the glow discharge process were utilized would, according to the data available at the present time, still be considerably higher.

How to obtain lower costs for a hydrazine discharge process is difficult to visualize but the data obtained during the study of the decomposition of ammonia may point a way. Employing high gas flow velocities the glow discharge allows the use of large amounts of power per reactor giving substantial outputs per unit time although the power efficiency is low. The corona discharge process studied at the Batelle Inst. had the advantage of operating at atmospheric pressure but the power input per reactor was small and its utilization was extremely poor. Electrodeless discharges in ozonizer-type reactors may offer a better possibility but again we run up against the difficulty of the relatively small amount of power that may be dissipated per unit of reactor surface area. It may, however, be possible to get around this difficulty in two different ways

either by increasing, separately or together, the frequency w of the applied electromotive force E and the capacitance C of the reactor. If the circuit contains the resistance R the current produced I is given by the equation:

$$I = \frac{E}{\sqrt{R^2 + 1/C^2 \cdot w^2}}$$

The resistance will decrease rapidly with the appearance of charge carriers passing through the gas phase of the reactor thus also increasing the strength of the current. The capacity C of a compound condenser consisting of two different dielectrics between two flat electrodes may, when fringe effects are neglected, be computed from the equation:

$$C = \frac{A}{4\pi (d_1/D_1 + d_2/D_2)}$$

where A is the contact area of one of the electrodes with the dielectric, d_1 and d_2 the thicknesses, D_1 and D_2 the respective dielectric constants of the dielectrics. If again one of the dielectrics represents a gas phase that becomes conducting and the other dielectric has a very high dielectric constant, like let us say barium titanate, near its Curie point where it approaches a value of about 10,000, an ozonizer-type reactor, which electrically is built like a compound condenser, may acquire a very high capacitance. Combining high frequency of the current with high reactor capacitance and relatively low resistance it should be possible to dissipate a large amount of energy in an electrodeless discharge.

In a glow discharge the major portion of the yield is formed in the positive column where most of the current is carried by electrons. The charge carriers in an electrodeless discharge are also mainly electrons and we could expect to find in this case approximately the same ratio between rates of formation and decomposition of hydrazine as in the case of the glow discharge. Thus although we would be able to dissipate a considerable amount of power uniformly over a large surface area, the degree of conversion of the ammonia to hydrazine would still be of the same order of magnitude as in the case of the glow discharge. However, if the yields of hydrazine obtained per KWH reactor power input would be about the same in both types of discharges, since the electrodeless type usually is run at ordinary pressures the work of compression from the low pressure that has to be used to obtain good power yields in a glow discharge, up to atmospheric would represent a considerable saving in total power costs. Part of the gain may naturally be offset by other losses like increased rate of decomposition of the ammonia. There is also another possibility that should be considered. Operating the silent discharge at a pressure of, let us say, 800 mm instead of about 20 mm for a glow discharge, the ease with which the hydrazine formed may be removed from the ammonia stream by absorption in a stationery bed of silica gel would be increased at least 40 times and still make the isolation of the hydrazine more feasible at reasonable cost. So far, however, we lack the experimental data required to decide on the merits of electrodeless discharges for the production of hydrazine from ammonia.

The Use of Electrical Discharges as a Tool For the Production of Various Chemical Compounds

The course of a reaction taking place in an electric discharge is dependent upon a number of different variables. Among the more important ones the following may be mentioned:

- 1) Nature and relative concentration of reactants. In case solids are used the average particle size is of decisive importance.
- 2) Type of discharge employed. This must be adjusted to the nature of the reactants and the product desired:
 - a) electrodeless discharge
 - b) glow discharge
 - c) pulsed DC discharge
 - d) high or low current arc
- 3) Characteristics of electromotive force applied (voltage, frequency and waveform) and strength of resulting current.
- 4) Flow velocity and degree of turbulence
- 5) Total pressure and pressure differential within reactor
- 6) Reactor design, this is in general determined by the type of discharge to be used and the kinetics of the reaction.

If otherwise suitable the nature of the electrodes employed seems as a rule to be fairly immaterial. In a large number of cases the only wall reactions that seem to occur are recombinations between the charge carriers with evolution of heat. Some of the earlier workers in this field and particularly K. Brewer supported an ion reaction mechanism theory and excluded the participation of excited atoms and molecules. However it has recently been shown by R.W. Lunt that there is no evidence from the data available for discharge reactions that charged particles are essential to the initiation, or to any other step, of the mechanism by which these reactions occur.

With this general background we will now enumerate some yield data for various reactions, studies of which are to be found in the literature. We will start with the formation of acetylene from other hydrocarbons. This reaction has been studied extensively over a period of many years in a large number of laboratories using both gaseous and liquid hydrocarbons. Uniformly astonishingly high power yields have been obtained. According to Schoch (Univ. of Texas public. No. 5011, June 1950) the overall amount of power required to produce one pound of acetylene using gaseous hydrocarbons is equal to 4.89 KWH, while in the case of liquid hydrocarbons only 3.55 KWH is needed. A power consumption practically identical with the latter value was obtained also by C.G. Suits (U.S. patent No. 2353770, July 1944) who employed ordinary mineral oils and established the discharge as innumerable short arcs between coke or carbon particles immersed in the oil.

Since methyl acetylene, which seems to have many desirable properties as a monopropellant or a rocket fuel, always is present in amounts of up to 2% of the acetylene formed in a discharge it would seem that this compound might be obtained at low cost and in large quantities by using a mild glow discharge with propane, or perhaps even better, with propylene as feed gas.

Silent electric discharges have been used particularly in Europe for polymerization reactions in lubricating oil type hydrocarbons. The processes taking place are exothermic and have probably the nature of chain reactions with a high degree of energy utilization. They are most economical when performed under vacuum with foaming so that the diameter of the

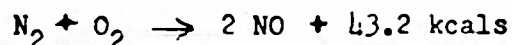
bubbles is somewhat larger than the mean free path of the oil molecules but smaller than the free path of the molecules of the inert gas led through. A review of the process has been given by Nash, Howard and Hall, J. Inst. Petroleum Techn. 20, 1027, 1934; c.f. H. Umstatter, Angew. Chemie, B 19, 207, 1947.

A number of studies of reactions of various hydrocarbons with compounds of other types are to be found in the literature. As examples will be mentioned the formation of hydrocyanic acid using aliphatic hydrocarbons and free nitrogen, the formation of aniline from benzene, ammonia and oxygen. In the case of hydrocyanic acid the yields obtained by Briner and Hoefer (Helv. Chim. Acta 23, 1054, 1940) in grams per KWH were using methane 60, butane 78, hexane 100 and octane 120. Under best conditions the concentration of HCN in the reactor exit gases was about 5% and the maximum energy utilization was 19%. According to P. Karrer (Organic Chemistry p. 438, Elsevier 1946) aniline is formed in the manner indicated above with yields of up to 15% per pass. Still another example of considerable interest is the direct oxidation of methane with oxygen studied by Briner and Hoefer (Helv. Chim. Acta 23, 800, 1940). They got formaldehyde yields of up to 16.6 grams per KWH with small amounts of acetylene produced simultaneously.

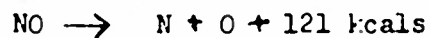
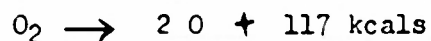
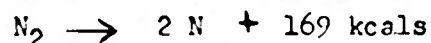
One of the chemical reactions first discovered to take place in electrical discharges was the formation of nitric oxide from air, but it is as yet far from completely understood and the experimental data obtained during its study are often contradictory. It seems fairly certain however

that in an arc or a glow discharge nitric oxide only is formed primarily and then the dioxide appears secondarily to be oxidized further to the pentoxide if ozone is present. A silent discharge in air produces mainly the latter compound and very little nitric oxide, while the reverse takes place in the former type.

A very complete review of earlier studies of the formation of nitric oxide in electric discharges is to be found in Gmelin-Kraut, Handb. anorg. Chemie, vol. Stickstoff, pp. 608-623, Germany 1938. Here we will give only a few of the more important details. The formation of nitric oxide is due mainly to a strongly endothermic reaction:



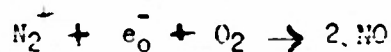
Since however di- and polyatomic molecules exposed to an electric discharge dissociate to produce free atoms and radicals, the effect of the following reactions should also be taken into consideration:



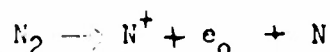
Thus the appearance of atomic nitrogen and oxygen would give a strongly exothermic reaction when they unite to form nitric oxide. The net result of the endothermic molecular and exothermic atomic reactions is that the concentration of nitric oxide formed will pass through a maximum as the temperature increases. Using an initially equimolar mixture of nitrogen and oxygen this maximum is at steady state equal to about 5.9% of nitric oxide at 3500°K.

Since the distribution of the electron velocities in the electrical field of the discharge is non-Maxwellian the concentration of an endothermic compound may attain much higher values than if a true thermal equilibrium solely dependent upon the temperature had been set up. Thus nitric oxide is produced in silent electrodeless and glow discharges at low temperatures and at concentration levels far above those demanded by the thermodynamic dissociation constant. It is also known that the concentration attained depends on pressure and discharge conditions which have nothing to do with the purely thermal reaction. The amount of nitric oxide formed in a discharge in ordinary air containing about 20% oxygen and 80% nitrogen is about 50% lower than the value found when a mixture of 30% oxygen and 20% nitrogen is employed under the same conditions although thermodynamically speaking they should be equal.

The exact mechanism for the formation of nitric oxide in an electric discharge has as yet been unraveled only partially. By electron bombardment experiments it has been found that a minimum electron energy of about 17 electron volts is required, which roughly corresponds to the ionization energy of the nitrogen molecule which is 15.7 electron volts. Thus the primary reaction would be the following one:



If the electron energy is raised to about 22 electron volts the yield of nitric oxide is highly increased. The higher electron energy corresponds to the reaction:



It makes both nitrogen ions and atoms available for the formation of nitric oxide. At the high electron energies given it should however also be taken into account that the oxygen molecules will dissociate and will in three body collisions or on a metal surface react exothermally with nitrogen atoms under formation of nitric oxide. As is well known, if air is exposed to short wave radiation oxygen is activated under formation of ozone. Thus the reaction of activated oxygen with nitrogen must be comparatively slow. Also, if this were not the case, the world we live in would look utterly different from what it does now. As a final conclusion, although the primary process in the formation of nitric oxide may consist of absorption of electronic energy by the nitrogen molecules this does not necessarily prove that ionized nitrogen is one of the reacting species. Simple excitation may be sufficient to cause reaction but it will be very difficult to decide one way or the other.

The yield of nitric oxide obtainable in a DC glow discharge is usually quoted as corresponding to about 80 grams of nitric acid produced per KWH. However very much higher yields of up to 160 grams have been claimed as possible by using high frequency currents.

When air or pure oxygen is subjected at ordinary pressures to a silent discharge ozone is formed. Several books have been written on what takes place during the formation, the properties and uses of this compound. It is highly endothermic and there is no other method known for its preparation except electrolysis of sulfuric or perchloric acids at very low temperatures. Since it is very effective as a water purifier and

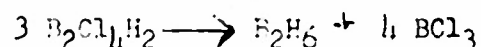
de-odorizer it has been employed primarily for this purpose in a number of large installations. If available cheaply in large quantities over short periods of time it would find extensive use in synthetic organic chemistry due to its ability to add to double bonds while giving quantitative yields of the products formed. According to Taylor and Bean (Eng. News Record, 143, No. 4, 32, 1949) the yield of ozone normally obtained in standard type industrial ozonizers is about 50 grams per KWH, but using high frequency current, yields several times larger have been claimed (Eriner and Deshusses, Helv. Chim. Acta, 13, 629, 1930).

It has been observed by Byrns and Rollefson (JACS, 56, 2245, 1934) that in blue light chlorine and ozone react to form chlorine heptoxide Cl_2O_7 in considerable quantities. The heptoxide is the most stable one of the chlorine oxides and would be suitable as an oxidant for rocket fuels since it is highly endothermic (-63.4 kcals) melts at -91.5°C and boils at about 80°C . The direct oxidation of chlorine in an ozonizer to form the heptoxide may also be a possible method for its production since Bodenstein, Padelt and Schumacher (Z. physik, Ch. B, 5, 209, 1929) found that during the reaction between wet chlorine and ozone, crystals of $\text{HClO}_4 \cdot \text{H}_2\text{O}$ were formed. The heptoxide hydrolysis to form perchloric acid HClO_4 .

A 2000 KW installation for the production of hydrogen peroxide in a silent discharge from wet hydrogen-oxygen mixtures has been described by M. Golden (Industrie Chimique 33, 153, 1946). The yield obtained in continuous operation was about 50 grams of hydrogen peroxide per KWH.

P.M. Wolf (Z. Elektroch. , 20, 204, 1914) found yields of about 17% of theory but at lower temperatures up to 99.9% of the oxygen was converted to peroxide. Penney and Sutjerland (Trans. Faraday Soc., 30, 898, 1934) and J. Chem. Physics, 2, 492, 1934) have deduced that the H-C-C-H molecule does not have free rotation around the C-C link and should have two tautomeric forms. Actually it has been found by Geib and Harteck (Berichte, 65, 1551, 1932), that if atomic hydrogen reacts with oxygen at liquid air temperatures a solid of the composition H_2O_2 is formed. This solid melts sharply at $-115^{\circ}C$ and starts to give off oxygen producing a liquid that at ordinary temperatures contains about 70% peroxide. This may perhaps be a feasible method to produce highly concentrated hydrogen peroxide solutions avoiding the more usual distillation methods.

According to Weintraub (U.S. Patent 1046043, Dec. 1910 and British Patent 25033, Oct. 1910) free boron with a high degree of purity may be produced by passing a mixture of boron trichloride and hydrogen gas through an electric discharge. At high current densities there is obtained a dense, crystalline mass which is very inert. In a mild glow discharge at low pressures an entirely different reaction can be induced to take place. As shown first by Schilling and Burg (Z.N.C., 53, 1321, 1931) and shortly afterwards by Stock and Sutterlein (Berichte, 67, 107, 1934) under these circumstances tetrachloro diborane is formed which subsequently decomposes under liberation of diborane:



The yields of diborane obtained by Schlesinger and his co-workers (JACS, 75, 191, 1953), were rather poor under the particular operating conditions chosen but it seems highly probable they could be improved substantially. At pressures above 20-30 mm Hg free boron is apt to separate out in a very finely divided, highly active form. Due to the high heat of combustion of boron, the heat of formation of the trioxide is 349 kcals, this may be of some interest with regard to the use of boron as a solid fuel. Perhaps it should also be added that a method has been found recently for the production of boron trichloride at low cost.

It has been demonstrated by Kroepeland Vogel (Zeitschr. anorg. Chemie, 229, 1, 1936) and others that compounds of heavy metals as a general rule are reduced with ease by atomic hydrogen. This might be of some interest with regard to the production of various metals directly from their concentrated finely powdered sulfidic or oxide ores. Among the heavy metals copper, lead, zinc, nickel, antimony, cadmium, molybdenum, vanadium and mercury are extracted principally from sulfidic minerals while for instance tin and tungsten usually are obtained from oxide ores. In the case of the former group, with a high rate of formation of hydrogen sulfide it may perhaps in some instances by burning the reactor exit gases be possible to generate sufficient power to keep the process running without any additional amount being required. The free metal content of the solid reaction product would be extracted by electrolysis and undecomposed sulfide recycled. This is only a suggestion and to reach a decision whether the scheme outlined has any practical value would naturally require a large amount of work.

From the data given above for the reactions discussed it would appear that with the proper choice of operating conditions yields may be obtained that in several instances are sufficiently high to warrant further study or possibly attempts at pilot plant operation. This is certainly the case with respect to acetylene which was amply demonstrated by Schoch (loc. cit.) using an apparatus able to produce from natural gas one ton of acetylene per hour. It would seem that it would be even simpler to maintain the same or even higher rates of production per reactor when liquid hydrocarbons are employed as raw material. The heavy metal sulfides or oxides have densities that are several times higher than those of the hydrocarbons. Provided the rate of reaction of atomic hydrogen with these compounds while passing through the discharge in a finely powdered state would be comparable with the rate of formation of acetylene, which however at the present time is a totally unknown factor, there does not appear to be any other distinct reason why throughputs of the same order of magnitude could not be employed in their case.

Plants producing ozone or hydrogen peroxide at rates of one ton per hour using electrodeless silent discharges would at present be major installations unless the power dissipation and simultaneously the rate of gas flow per unit time and per reactor could be increased by an order of magnitude without changing their size or the yield per KWH. A step in this direction is indicated by a patent issued to T. Rummel (German 696081, Aug. 1940) who found that by coating either one or both of the electrodes with titanium or zirconium dioxide the yield of ozone was greatly increased. The different crystal forms of titanium dioxide

(rutile, anatas and brookite) have all relatively high dielectric constants. Therefore still higher yields may perhaps be obtainable by using as solid dielectric barium metatitanate which near its Curie point has a dielectric constant in the neighbourhood of 10,000 (c.f. discussion for the formation of hydrazine in silent discharges).

The particular compound that may be synthesized in an electric discharge of a given type by introducing a pure substance or a mixture of two or more different ones, may so far be determined by experience only. The number of different reactions studied or for which data are available is too limited to allow any more than the most general predictions of the outcome as based on our knowledge of what to expect to happen under ordinary circumstances with the added possibilities due to excitation and ionization processes of the participating molecules. As an example we could expect the highly endothermic compound chlorine monoxide to form in a silent but not in a glow discharge from a mixture of free chlorine and oxygen. Subsequent reactions following the initial formation of the monoxide may, in the case of the presence of ozone formed simultaneously probably give first chlorine tetroxide Cl_2O_4 and then the heptoxide Cl_2O_7 .

Conclusions and Summary

Our study is in many respects incomplete and undue emphasis may have been given to various aspects. From the start it was known all we could hope for was that only a minor share of the total amount of power dissipated in the discharge would be utilized for the formation of hydrazine.

We also knew that when the discharge was operated at low pressures and at minimum sustaining energy the reforming of ammonia decomposed would represent only a fraction of the total power consumption.

The method immediately available for varying the discharge power input over a wide range was to employ a glow discharge and the actual procedure followed seemed to be the most natural one as long as it was unknown if any other one would have given better results. Therefore the study of the formation of hydrazine in electrodeless discharges was not pursued beyond ascertaining that it was formed in appreciable quantities. The comparatively very small amount of power that could be dissipated in even fairly large reactors of the type employed made further work in this direction appear unprofitable. However, as pointed out above, if it were possible to build a reactor of the type in question using a dielectric with a dielectric constant of about 10,000 instead of that of ordinary glass, which is about 3, we are looking at an entirely different aspect of the problem. It would then be possible to dissipate large amounts of power, to operate a number of cells in parallel without complicated controls, to employ sizable ammonia flows, to use ordinary or slightly higher pressures, to isolate the hydrazine formed in stationary absorbent beds. With the reactor given its usefulness for large scale production of hydrazine could be decided with a few simple tests.

As stated above, on account of the low cost of ammonia, the reforming cost of ammonia decomposed in the discharge would only be a fraction of the total power cost. It had further been found that even when fairly large

quantities of nitrogen and hydrogen were added to the ammonia stream the changes observed in the hydrazine yield could be attributed mainly to a dilution effect. Thus it seemed at the time that until the practical usefulness of the formation of hydrazine in a glow discharge had been definitely established, the amount of ammonia decomposed was fairly unimportant. However the data obtained by Dr. Honig seem to throw a somewhat different light on the function of gases added.

The study of the kinetics of the formation of hydrazine showed first of all that the rate of decomposition is more than four hundred times larger than the rate of formation. The high rate of decomposition limits the apparent degree of ammonia conversion attainable to a very low level that could be changed very little regardless of the operating conditions. The second most important result was the extremely high reaction rates found, necessitating the use of contact times between discharge and ammonia stream of a few milliseconds in order to get maximum power yield and minimum waste of energy. The third main result of the kinetic measurements revealed the extreme importance of getting intimate contact between the electric plasma and the streaming ammonia gas. Unless this could be accomplished adequately both the degree of ammonia conversion and the yields of hydrazine per kWh were lowered.

This started off attempts to design a reactor where plasma and ammonia mixed efficiently. Reactors designed to allow the ammonia stream to flow through a conical cavity with solid glass walls producing an angular velocity rapidly increasing towards the exit, did not give the desired result.

Substituting the solid walls for slightly overlapping, evenly spaced baffle discs generated a uniformly dispersed, voluminous discharge, but it was difficult to get the reactor to function properly over longer periods of time due to incessant dielectric breakdown. Simultaneously we had started experiments with helically fluted, tubular reactors with a double thread at 180° angle to each other making the ammonia stream perform a weaving or braiding motion around the electric plasma. In the case of fairly narrow reactors this method of approach appeared to give excellent results and a whole series of increasingly larger ones were made up. The large reactors however did not give good yields and it became apparent that in the case of large ammonia flows it would be necessary to spin the gas around in some other manner. Thus we returned to the use of the conical cavity which this time was mounted on top of the reactor and served to give the gas stream a very high angular velocity before it entered the reactor proper. The center of the latter was occupied by a water cooled tube and the ammonia gas spun around in the narrow annular space between this tube and the enclosing glass mantle. Using a 24 inches long glass pipe of 4 inches inner diameter and having an annular space about $1/4$ inch wide it was found that a very uniform discharge could be obtained even at moderate ammonia flows and without exposing the wall of the mantle tube to larger temperature increases.

Early in our work we had tried out a number of different additives to the ammonia stream but not a single one of them had been found to be of any value. The wall effect on the hydrazine yield obtained seemed to be negligible. Finally we also tried water as an additive. In the case

of the reactor employed and particularly at lower pressures the degree of ammonia conversion improved greatly although the hydrazine yield per KWH decreased, presumably due to power losses in the liquid phase.

The study of the decomposition of ammonia showed some very remarkable results particularly when helium was added to the ammonia. Under certain conditions ammonia conversions up to 3.4% were obtained as compared to the usual values of 0.2-0.3%. The maximum power yield attained was 22 grams per KWH, but similar values had previously been measured with pure ammonia and during a talk given at the ACS meeting in Los Angeles March 15-19 by Professor M. Burton of Notre Dame University he claimed to have gotten approximately double the maximum yields indicated here although his values for the degree of ammonia conversion were very low. In view of these data it is premature to give a final decision with regard to the practicality of the use of glow discharges for the production of hydrazine from ammonia. Therefore it is recommended that: 1) an engineering study be made of all data available, 2) proposed designs for large reactors are critically reviewed, 3) some further measurements be made with flows in the range 2-6 CFM or higher under flow conditions adjusted to give high yield and degree of conversion 4) a limited study be made of electrodeless discharges employing reactors with dielectrics having high dielectric constants.

APPENDIX I.

The Formation of Electric Discharges

Under normal conditions all gases are non-conductors and passage of a sustained electric current can occur only when charge carriers like electrons and ions are produced continuously and conduction established by the influence of an applied field. Ionization in a gas takes place either by transfer of kinetic energy from the charge carriers to neutral molecules in non-elastic collisions or by their absorption of radiation. The energy E transferred at the time of ionization, either by collision or radiation, must be at least as large as the ionization energy I of the atoms or molecules involved. In addition to this condition the rate of ion formation depends also on the ionization probability which is a function of the amount of energy transferred.

In case ionization is caused by radiation the energy of the photon must be equal to or larger than I . Thus the wave length limit at which ionization may occur is given by the equation:

$$\lambda = \frac{h \cdot c}{I} \quad (1)$$

where c is the velocity of light. Introducing known values for I in equation (1) it is readily found that only radiation of very short wavelengths like X-rays is able to cause ionization. If the energy of an electron released by radiation is very large it can then give rise to collisional ionization of several atoms or molecules, until its velocity has decreased to the minimum value necessary.

Let us now assume that N_0 primary electrons released per unit area and unit time at the cathode in a homogeneous field produce secondary electrons per unit length of its path towards the anode. Over the distance dx the number of electrons added dN will be equal to:

$$dN = N \cdot a \cdot dx \quad (2)$$

Integrating over the entire distance r between the electrodes the total number of electrons arriving at the anode per unit time is given by the equation:

$$N_r = N_0 \cdot e^{ar} \quad (3)$$

The current amplification factor f due to collisional ionization is thus equal to:

$$f = e^{ar} \quad (4)$$

The value of a , which has been called the first Townsend coefficient, is proportional to the number of collisions per unit length and thus also the pressure p of the gas. It is also dependent on the kinetic energy attained between two successive collisions. This energy is proportional to the product of field strength F and mean free path. Empirically a is related to F and p by the equation:

$$a = p \cdot A \cdot e^{-B \cdot p / F} \quad (5)$$

where A and B are constants characteristic of the gas employed.

Thermal production of charge carriers is due to increased energy of collision between atoms and molecules with increasing temperature. Ions and electrons produced are more efficient than neutral molecules in bringing about further ionization, but as they undergo recombination reaction an equilibrium dependent upon the temperature is set up. The equilibrium has been evaluated according to ordinary chemical kinetics and may be expressed by the equation of Saha:

$$p \frac{\alpha^2}{1 - \alpha} = \frac{(2 \pi m_e)^{3/2} (kT)^{5/2}}{h^3} \cdot e^{-I/kT} \quad (6)$$

where α is the degree of ionization of the gas, p the pressure, m the mass of the electron, T absolute temperature, h and K Planck and Boltzmann constants respectively.

By heating various electronic conductors like metals, their oxides and nitrides etc., the energy of their electrons may be raised above the level of the thermionic work function. The fraction having sufficient energy to escape increases with temperature and the thermionic current i may be calculated from the known energy distribution in the electron gas according to an equation derived by Richardson:

$$i = A T^2 \cdot e^{-W/kT} \quad (7)$$

where W is the thermionic work function and A is a constant which in the case of pure metals may vary between 60 to 100 amperes per square cm degree.

Selfsustained Discharges in Gases

In a self-sustained discharge, after the initial formation of the charge carriers by one of the methods described above, the arc is maintained in the gas phase by the applied field itself. If the potential between the electrodes is sufficiently high to cause collisional ionization to occur, the current increases rapidly with the potential. From equations (4) and (5) we find that, assuming as before a homogeneous field, the amplification factor f is given by the equation:

$$\ln f = A \cdot p \cdot r \cdot e^{-B \cdot p / F} \quad (8)$$

Both at very low and very high pressures $\ln f$ approaches a value of zero and no amplification occurs since f then is equal to unity. In the former case the mean free path of the electrons is so large that only infrequent collisions with the gas molecules occur, while in the latter one the free path is too short to allow sufficient energy gain between collisions to cause ionization. Thus f must pass through a maximum at some pressure p_0 obtained by differentiation of (8):

$$F_0 = F / B \quad (9)$$

As has been verified experimentally p_0 is thus proportional to the field strength. As the latter increases the velocity and kinetic energy of the charge carriers also increase continuously. When large enough to cause ionization of the gas molecules, and the number of positive ions formed is sufficient to release other electrons at impact with the cathode, new charge carriers are liberated and they in turn produce more ions by collision in avalanche fashion causing a rapid increase in current i according to the equation:

$$i = N_0 \cdot e_0 \cdot e^r \quad (10)$$

where e_0 is the electronic charge. We may now state the conditions necessary to obtain a self-sustaining discharge. Negative charge carriers consisting of electrons and negative ions are discharged at the anode. The energy liberated there is converted mainly to heat and no emittance of charge carriers takes place at the anode. The cathode absorbs all the positive ions but it will also emit electrons provided these ions can impart to them energy in excess of the cathode work function. When each electron liberated at the cathode, on its passage through the gas phase causes the emittance of at least one more electron from the cathode, a selfsustaining discharge has been started. Just like the primary electrons, the secondary ones accelerate in the electric field, acquire sufficient kinetic energy to release one or more other electrons in new collision processes. Quantitatively the condition necessary for the start of a selfsustaining discharge may be obtained from equation (3) provided account is taken of the energy transported back to the cathode by the positive ions formed. As before, let us assume that N_0 primary electrons produce $N_0 \cdot e^{r-1}$ at the anode. Of these $N_0 \cdot e^{r-1} - N_0$ are formed in the gas phase as secondary electrons together with an equal number of monovalent positive ions. Every one of the positive ions yields an average of X new electrons at the cathode emitting at least one more electron per original electron emitted:

$$X (e^{r-1} - 1) = 1 \quad (11)$$

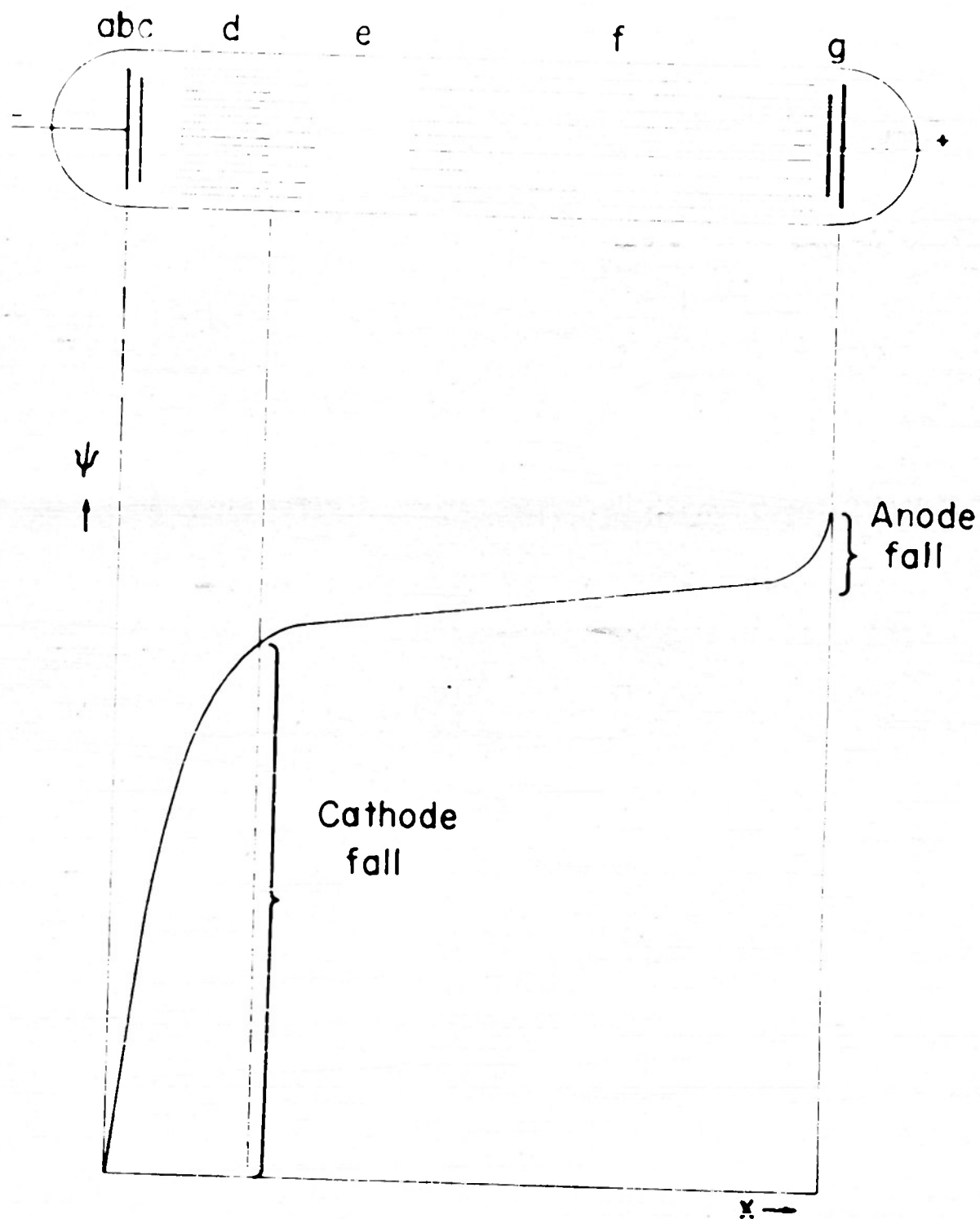
This equation expresses the condition that must be fulfilled to obtain a self-sustaining discharge.

Glow Discharges

In our study of the formation of hydrazine from ammonia, glow discharges have been used exclusively and due to this reason their behavior will be discussed in some detail. To understand the phenomena that occur in these discharges it is necessary to take into account the fact that the electrical field between flat, parallel electrodes is strongly distorted. The discharge itself consists of a series of luminous layers and dark spaces which are particularly well developed when pure noble gases are present.

The Aston dark space (a in Fig. 1) is a very thick layer at the cathode. The primary electrons released from the cathode and passing through this layer have as yet insufficient kinetic energy to cause excitation of the surrounding gas molecules. In the cathode glow (b) the energy of these electrons is sufficient for collision excitation, making the gas luminous. Spectral lines appear in the order of increasing excitation energies in the direction of the anode.

In Crooks dark space (c) the primary electrons have acquired such a high kinetic energy that the excitation probability has started to fall off, decreasing the amount of radiation given out. The boundary (d) of the negative glow towards the cathode is fairly well defined while the luminosity decreases in the direction of the anode. To the primary electrons are added large numbers of secondary ones, and positive ions creating the so-called plasma which retards the electrons and spectral lines appear in decreasing order of their excitation energy. When the



POTENTIAL-DISTANCE RELATION
IN A GLOW DISCHARGE

electrons arrive in the Faraday dark space (e) they have lost so much kinetic energy that they are unable to excite the gas molecules.

The positive column (f) is the largest and most luminous section of the entire discharge. In this region the potential gradient is small and almost the entire current is carried by the electrons. Depending upon the pressure and the nature of the gas present, the positive column may either be practically uniform, striated or consist of luminous band with dark spaces between them. The anode glow (g) is due to collisional ionization by the electron shortly before they reach the anode.

The potential in the discharge drops steeply in the region between the cathode and the negative glow but changes from then on, and practically to the end of the positive column, slowly and linearly. Close to the anode the potential drop is again fairly pronounced. The discharge current is carried mainly by transport of electrons and positive ions. The kinetic energy they acquire over the potential drop Δp is given by the equation:

$$e_0 \Delta p = m u^2 / 2 \quad (12)$$

where e is the electronic charge, m and u mass and velocity respectively. If the atomic or molecular weight of the positive ions is A the velocity attained by the electrons should be $\sqrt{1840A}$ times larger than that of the ions. However, due to their small size the actual difference is much larger and kinetic theory gives the value $102 \sqrt{A}$ as the ratio between the velocities of electrons and positive ions. This large difference gives rise to the so-called space charge and the potential distribution in the discharge indicated above.

Neglecting the presence of the primary electrons in the plasma of the positive column the number of electrons is equal to that of the positive ions since in each ionization process both a positive and a negative charge carrier is produced. The plasma is therefore electrically neutral and free from space charge. The total current i is given by the equation:

$$i = i_+ + i_- = e_0 \cdot N_+ \cdot u_+ + e_0 \cdot N_- \cdot u_- \quad (13)$$

Since $N_+ = N_-$ and $u_- / u_+ = 102$ we obtain:

$$i_- / i_+ = u_- / u_+ = 102 \quad (14)$$

Thus the current carried through the plasma by the electrons is over 100 times larger than the portion transported by the positive ions.

REFERENCES

1. W. H. Anderson, B. J. Zwolinsky, and R. R. Parlin: Technical Report IV to the Atomic Energy Commission; University of Utah, Salt Lake City, Utah, 1952.
2. V. A. Bailey and W. E. Duncanson: Phil. Mag. 10, 145 (1930).
3. W. H. Bair; Astrophys. Jour. 52, 301 (1920).
4. J. H. Bartlett: Phys. Rev. 33, 169 (1928).
5. M. A. Besson; Compt. Rend. 152, 1850 (1911).
6. K. F. Bonhoeffer and L. Farkas: Z. phys. Chem. 134, 331 (1928).
7. N. E. Bradbury: J. Chem. Phys. 2, 827 (1934).
8. G. Bredig, A. Koenig, and O. H. Wagner: Z. phys. Chem. A139, 211 (1928).
9. E. Bruche: Ann. d. Phys. 1, 93 (1929).
10. H. Chauvin and S. Leach: Compt. rend. 231, 1462 (1950).
11. J. H. Davis: Z. phys. Chem. 64, 657 (1908).
12. J. K. Dixon: Phys. Rev. 43, 711 (1933).
13. J. K. Dixon and W. Steiner: Z. phys. Chem. B17, 327 (1932).
14. A. B. F. Duncan: Phys. Rev. 47, 822 (1935).
15. A.B.F. Duncan: Phys. Rev. 47, 886 (1935).
16. A.B. F. Duncan: Phys. Rev. 50, 700 (1936).
17. A. B.F. Duncan and G. R. Harrison: Phys. Rev. 49, 211 (1936).
18. H. A. Erikson: Phys. Rev. 30, 339 (1927).
19. L. Farkas, F. Haber, and P. Harteck: Z. Elektrochem. 36, 711 (1930).
20. M. W. Feast; Astrophys. Jour. 114, 344 (1951).
21. M. W. Feast: Proc. Phys. Soc. London A63, 563 (1950).
22. Ferrières: Comp. Rend. 178, 202 (1921).
23. A. Findlay: Z. Elektrochem. 12, 129 (1906).
24. H.H. Franck and H. Reichard: Naturwiss. 24, 171 (1936)

BEST
AVAILABLE
COPY

25. G. W. Furke: Z. f. phys. 96, 787 (1935).
26. G. R. Gedge: Trans. Faraday Soc., 27, 474 (1931).
27. G. Gehlhoff: Ann. d. Phys. 24, 553 (1907).
28. J. Janin: J. Rech. Centre Natl. Rech. Sci., 12, 156 (1950).
29. J. Janin and A. Crozet: Ann. Univ. Lyon Sci., B4, 2 (1948).
30. J. Janin and A. Crozet: Comp. Rend. 223, 1114 (1946).
31. H.O. Kneser: Ann.d. Phys. 79, 585 (1926).
32. A. Koenig and L. Brings: Z. phys. Chem. Bodenstein Festband, 541 (1931).
33. A. Koenig and O. H. Wagner: Z. phys. Chem. A144, 213 (1929).
34. R. Kollath; Phys.Zeitsch. 31, 985 (1930).
35. G. I. Lavin and J. R. Bates: Nature 125, 709 (1930).
36. G. I. Lavin and J. R. Bates: Proc. Nat. Acad. Sci. 16, 804 (1930).
37. M. LeBlanc: Z. Elektrochem. 14, 261 (1908).
38. M. LeBlanc: Z. Elektrochem. 14, 507 (1908).
39. S. W. Leifson: Astrophys. Jour. 63, 73 (1926).
40. E. P. Lewis: Astrophys. Jour. 40, 154 (1914).
41. R. W. Lunt and J. E. Mills: Trans. Faraday Soc. 35, 786 (1935).
42. R. W. Lunt, J. E. Mills, and E. C. W. Smith: Trans. Faraday Soc. 31, 792 (1935).
43. R. W. Lunt, R. W. B. Pearse, and E. C. W. Smith: Nature 136, 32 (1935).
44. C. A. Mackay: Phys. Rev. 24, 319 (1924).
45. E. M. Mann, A. Hustrulid, and J. Tate; Phys. Rev., 58, 349 (1940).
46. G. Nakaya and H. Tanaka: Japanese Jour. Phys. 10, 5 (1936).
47. G. Nakaya and H. Tanaka: Z. Elektrochem. Ass. Japan 17, 285 (1949).
48. J. Pohl: Ann. d. Phys. 21, 873 (1906).
49. J. Pohl; Z. Elektrochem. 14, 439 (1908).

50. E. Regener: Ann. d. Phys. 20, 1033 (1906).
51. E. H. Riesenfeld: Z. Elektrochem. 17, 725 (1911).
52. ... Rimmer: Proc. Roy. Soc. London A103, 696 (1923).
53. N. Sasaki and Y. Ohta: J. Chem. Soc. Japan 63, 1491 (1942).
54. N. Sasaki and Y. Ohta: J. Chem. Soc. Japan 63, 1496 (1942).
55. K. Schäfer and R. Conrad: Z. f. Physik 107, 393 (1937).
56. G. M. Schwab: Z. anorg. allg. Chem. 236, 296 (1938).
57. V. Spreter and E. Briner: Helv. Chim. Acta 32, 2044 (1949).
58. V. Spreter and E. Briner: Helv. Chim. Acta 32, 2524 (1949).
59. T. M. Sugden, A. D. Walsh, and W. C. Price: Nature 148, 372 (1941).
60. P. Swings, A. McKellar and R. Minkowski: Astrophys. Jour. 98, 142 (1943).
61. R. J. Thomson and A. B. F. Duncan: J. Chem. Phys. 14, 573 (1946).
62. A. T. Waldie: J. Franklin Inst. 200, 507 (1925).
63. E. Warburg: Z. Elektrochem. 27, 133 (1921).
64. J. W. Westhaver: J. Phys. Chem. 37, 897 (1933).
65. E. J. B. Willey: Trans. Faraday Soc. 30, 230 (1934).
66. E. J. B. Willey: Trans. Faraday Soc. 39, 234 (1943).

THE FORMATION AND DECOMPOSITION OF HYDRAZINE

IN A STEADY D. C. DISCHARGE

by

R. D. Goodwin and J. M. Honig

TABLE OF CONTENTS

	Page
Preface	i
Abstract	ii
1. Introduction	1
2. Experimental Methods	2
A. Apparatus and Manipulation	2
Procedures; Formation of Hydrazine	4
Procedures; Decomposition of Hydrazine	6
B. Materials	6
C. Analytical Method for the Determination of Hydrazine	9
D. Computation of Experimental Results	11
Computations Involving Fundamental Data	11
Computations Involving Derived Quantities	12
Precision of Results Involving the Quantity y	16
3. Decomposition of Ammonia	17
A. Pure Ammonia; Decomposition into Noncondensable Gases	17
B. Hydrazine Synthesis from Pure Ammonia	18
C. Decomposition of Ammonia in the Presence of Water Vapor	27
D. Ammonia Decomposition in the Presence of Nitrogen and Hydrogen	28
General Discussion	28
Decomposition of Ammonia into Noncondensable Gases	30
Decomposition of Ammonia into Hydrazine	34
E. Ammonia Decomposition in the Presence of Helium	38
Decomposition of Ammonia into Nitrogen and Hydrogen	38
Decomposition of Ammonia into Hydrazine	38
4. Decomposition of Hydrazine in Discharges, Using Ammonia, Nitrogen, Hydrogen or Helium as Carrier Gases	44
A. Introduction	44
B. Decomposition as a Function of Power Input	44
C. Decomposition Products	50
5. Discussion	52
A. Absolute vs. Relative Conversion	52
B. Synthesis and Decomposition of Hydrazine in the Discharge	54
6. Summary	54

PREFACE

This report describes experimental work performed by the authors at The James Forrestal Research Center of Princeton University from January through June, 1953, under Office of Naval Research Contract N6onr-27017.

The objectives of this program were to examine the effects of several practical variables relating to the synthesis of hydrazine from ammonia in an electric discharge. In order to carry out this study as rapidly and economically as possible, laboratory bench-scale apparatus was employed in place of the large scale equipment used previously.

ABSTRACT

The decomposition of ammonia into hydrazine, hydrogen and nitrogen under the action of a steady discharge has been studied. The effect of power input, flow rate, reactor pressure, and presence of inert diluents on the formation of the discharge products has been investigated. The decomposition of hydrazine in the discharge was also studied.

The results of this investigation are summarized in section 6.

1. INTRODUCTION

The decomposition of ammonia in electric discharges has been discussed extensively in the literature.* A survey of this work shows that the process is exceedingly complicated. Various investigators have detected the presence of NH_3 , N_2H_4 , NH_2 , NH , N_2 , H_2 , and H ; also, the presence of a large number of positive and/or negative ions. Under such circumstances a wide variety of opinions can be expected as to the nature of the steps which lead to the formation of hydrazine or of nitrogen and hydrogen in the discharge.

The extent of decomposition of ammonia into hydrazine as a function of various discharge conditions has also received considerable attention in the literature and on this project. It has always been found necessary to use a flow system in order to produce more than minute traces of hydrazine from ammonia. Even under most favorable conditions of operation the mole fraction of hydrazine in the product did not exceed 0.01 in any of the work published to date; the best power yields reported so far are in the range 5 to 15 grams of hydrazine per kilowatt hour of electrical energy. The production of hydrazine relative to hydrogen and nitrogen seems to be favored by use of the lowest possible power inputs which will just maintain the discharge.

*For details consult the review of the literature presented in the final report covering work performed under the present contract.

Despite all of the work reported in the literature a systematic investigation of the relative decomposition of ammonia into hydrazine or into the elements as a function of power input, flow rate, and diluents in a steady discharge is still lacking. It was therefore considered important to initiate such a study.

2. EXPERIMENTAL METHODS

A. Apparatus and Manipulation

Bench scale apparatus used in the present investigation is shown schematically in fig. 1. The discharge reactor may be identified by the plus and minus markings of the electrodes. The reactor, of pyrex glass, was 0.8 cm inside diameter and 45 cm in length. It was surrounded by a water jacket. Copper electrodes were inserted in the enlarged ends of the tube with their tips 47 cm apart, and were held in place by means of vacuum tight rubber stoppers. The bottom electrode was grounded and was water cooled. The gas products flowed past this electrode before reaching the exit.

Gases were introduced at measured flow rates from the manifold at the left of the reactor. After passing through the discharge most of the emerging gas was withdrawn through the large pressure regulating stopcock by means of a high speed mechanical pump. A small portion of the emerging gas was allowed to pass into the manifold of the high vacuum analytical system to the right of fig. 1.

Ammonia, nitrogen, hydrogen, and helium were introduced from the cylinders of compressed gases through appropriate reducing valves and atmospheric pressure rotameter-type flowmeters. Water vapor and hydrazine vapor could be admixed with these gases from individual reservoirs with associated capillary leaks thermostated with boiling water at 100°C, (See fig. 1). The rate of effusion of these vapors could be determined by leading them into the first cold trap of the analytical train. The weight of condensate was measured after a predetermined time interval.

Three five liter flasks of type "A" served to collect aliquot portions of the gas mixture emerging from the reactor. The bulbs were removed to the analytical laboratory for hydrazine analysis. Two two liter flasks "B" received another portion of the product gases. After isolation from the manifold the cold finger of these bulbs was immersed in liquid nitrogen to freeze out all condensable gases. Those gases which remained in the gas phase after this treatment are labelled "noncondensable gases" throughout this report.

Mercury manometers were used for pressure measurements. The pressures at the top and bottom of the discharge tube were measured using a U tube manometer with a range up to 200 mm Hg. Gas pressures in the analytical train were usually determined with one of the two McLeod gages sketched in fig. 1. One covered the range 0.002 to 2.5 mm Hg, the other, the range 0.2 to 40 mm Hg. A coarse rotary gage for rapid readings in the range 0.02 to 10 mm Hg and an absolute U tube manometer for readings up to atmospheric pressure were also provided. The analytical line was evacuated with a mercury diffusion pump and a mechanical forepump.

In examining the results of the next few sections it must be kept in mind that under the experimental conditions the pressure at the top of the reactor was always higher than that at the bottom. Depending on operating conditions, these pressure differences varied from 10 to 100 per cent of the pressure at the bottom. The discharge therefore, emerged as a narrow thread from the top electrode high pressure region and filled essentially the entire cross section of the reactor near the bottom electrode. The poor definition of the discharge might have been eliminated by careful redesigning of the reactor tube but corrections were not undertaken due to shortage of time and because it was desirable to compare present results with those obtained earlier on the project using similar tubes.

A power supply manufactured by the American Transformer Company, capable of an output of 20 KV and 800 ma was used to maintain the discharge. The output was passed through two Eimac VT 129/ 304 TL current limiter tubes to the electrodes.

Procedures; Formation of Hydrazine:

The following procedure was employed: The analytical vacuum line and sample bulbs were evacuated to a pressure of less than one micron. After isolation from the pumps pressure line was checked five minutes later to test for leaks. If there were none the flow of gases through the mixing manifold and the reactor tube was started. The rate of flow was regulated by use of the flow meters and pressure control was achieved by means of the large connecting stopcock to the high speed mechanical pump. The discharge was allowed to operate for three minutes

and a portion of the effluent gases was then admitted to the analytical system for a period of approximately two minutes. The gas pressure in the analytical line (usually 5 mm Hg) was determined with the high pressure McLeod gage. This measurement is termed the "sample pressure" of the run in subsequent sections.

Flasks "A" and "B" were then isolated from the line and flask "A" was sent to the analytical laboratory for hydrazine assay according to the procedure detailed in section 2A. The cold finger of flask "B" was immersed in liquid nitrogen, while the rest of the analytical manifold was evacuated. After thirty minutes the residual pressure of the gases that had not been condensed was measured with a McLeod gage. This measurement will be referred to as the "noncondensable gas pressure".

When diluents were used, or in the experiments of section 4, a further set of measurements was required to ascertain the composition of the starting mixture. For this purpose a blank sample was taken in the absence of the discharge as soon as possible after the regular sample, leaving all flowmeter settings unaltered. With duplicate sample bulbs on the vacuum line this could be achieved within three minutes of the regular sample.

A waiting period of thirty minutes sufficed to freeze out all the noncondensable gases in flask "B". This fact was established at the conclusion of run 20, at which time both McLeod gages were filled with a mixture of the reaction products containing ammonia, hydrazine, and

hydrogen plus nitrogen in the ratio 470: 1 : 30 at a pressure of 19 mm Hg. The cold finger was immersed in the liquid nitrogen bath at time zero and the pressure drop in the system of flask "B" and the two McLeod gages followed. The results are shown in fig. 2, indicating that after thirty minutes there was no further decrease in the pressure.

Procedures; Decomposition of Hydrazine: The decomposition of hydrazine in various diluents (section 4) was studied by passing the mixture through the discharge tube and collecting an aliquot sample in flask "A" for analysis. A blank in the absence of the discharge was run to ascertain the composition of the starting mixture.

B. Materials

Ammonia in 150 pound net cylinders from the Polychemicals Department of E. I. du Pont de Nemours & Company, labelled "Anhydrous Ammonia, National" was employed in this work. The water content is stated to be negligible. Blank runs in the absence of the discharge showed that the amounts of noncondensable gases and of hydrazine in the ammonia were negligible.

Hydrazine from the Fairmount Chemical Company, 600 Ferry Street, Newark 5, New Jersey, was used in the experiments of section 4. This material was labelled "Hydrazine Base 95%", the remaining 5% were presumably water.

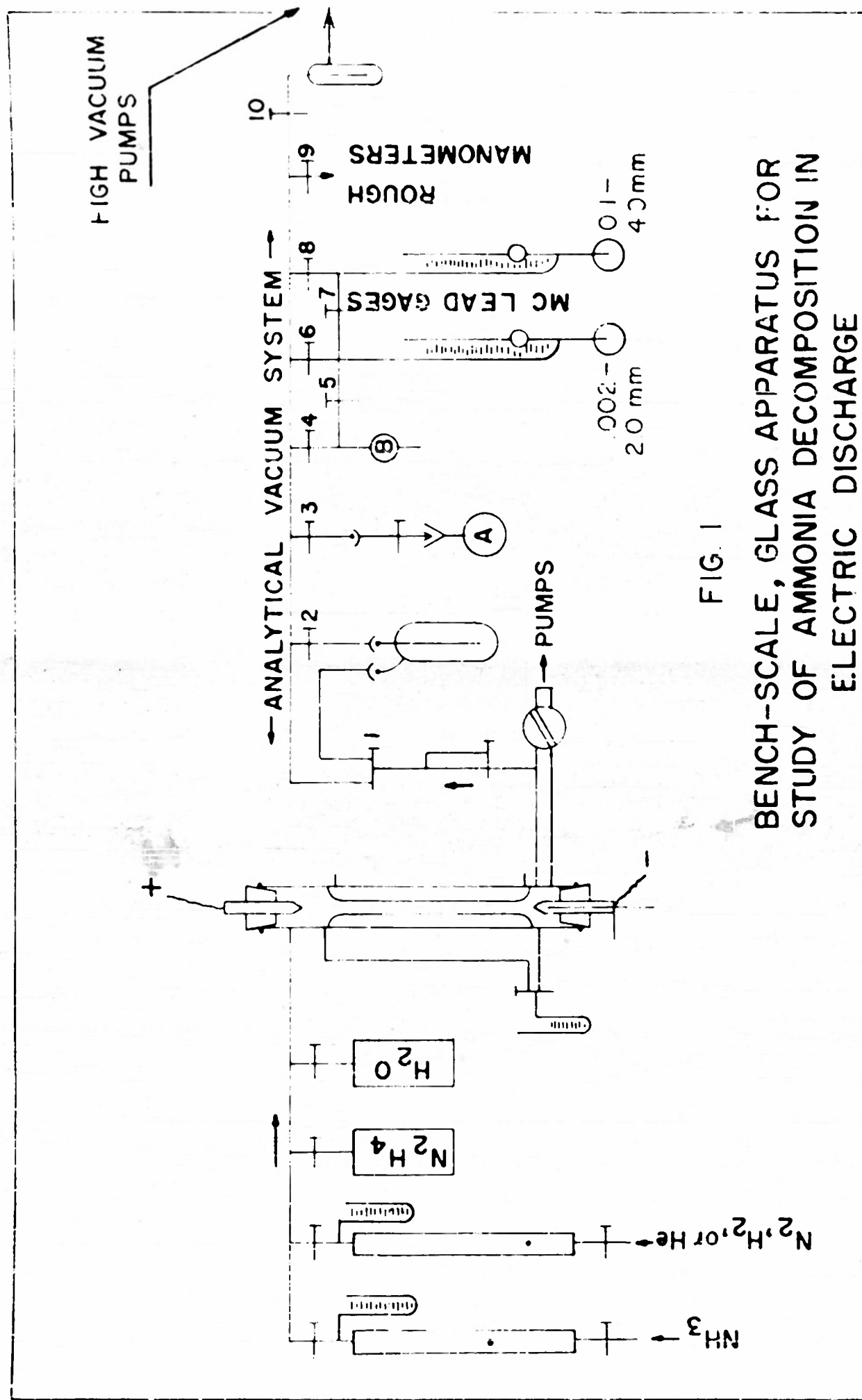
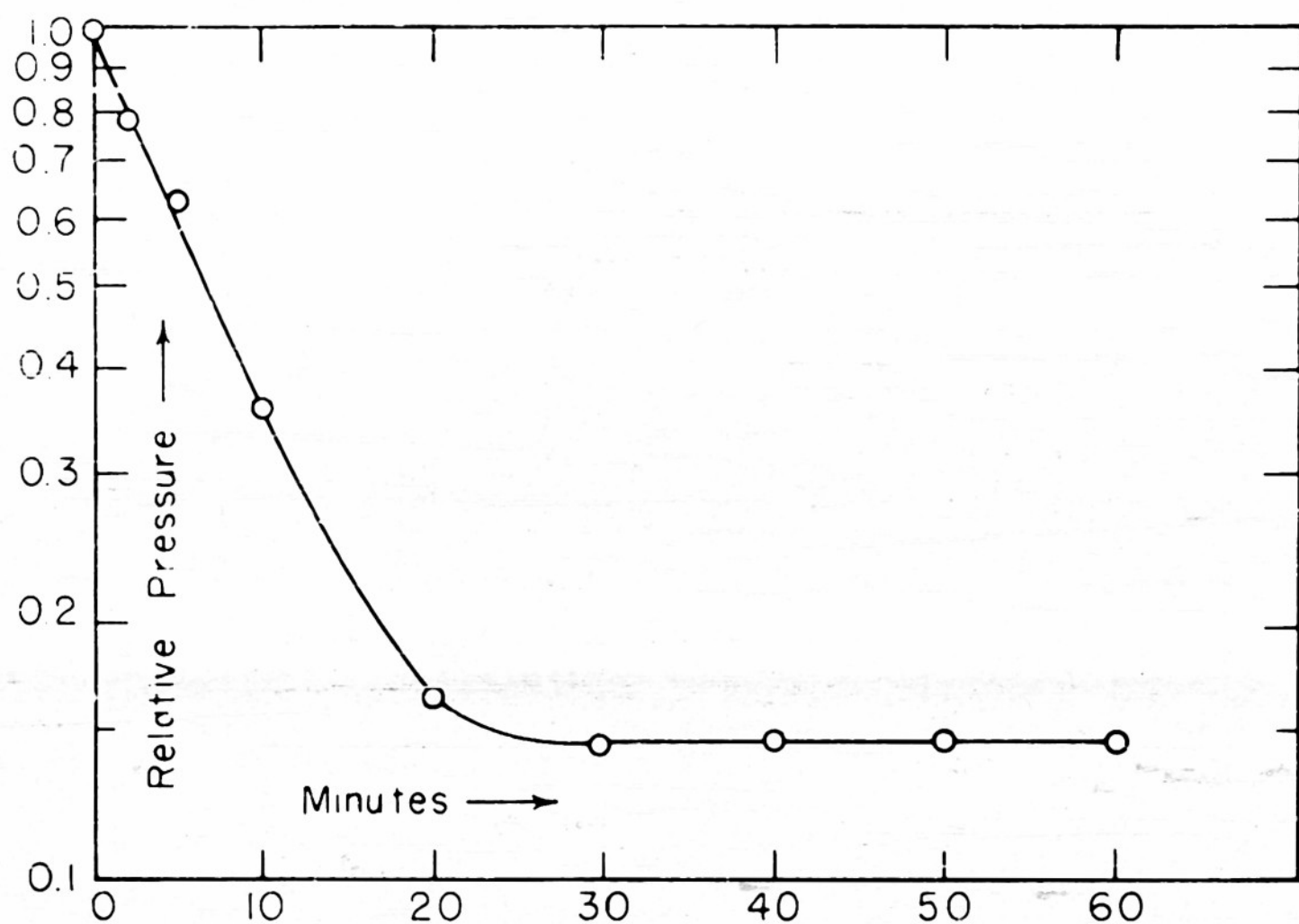


FIG. 1

BENCH-SCALE, GLASS APPARATUS FOR
STUDY OF AMMONIA DECOMPOSITION IN
ELECTRIC DISCHARGE



Freezing-Out of NH_3 from Products of
 NH_3 Electric Discharge

Final Pressure = 2.8mm Hg.

Figure 2

Hydrogen was supplied by the Matheson Company, East Rutherford, New Jersey, with a purity of 99.8%.

Nitrogen of "prepurified grade" and helium were supplied by the American Oxygen Company, Harrison, New Jersey. The purity of these gases was stated to be 99.9%.

C. Analytical Method for the Determination of Hydrazine

Samples for analysis were received in 5 liter bulbs at reduced pressure. 100 cc of approximately 0.1 M hydrochloric acid was admitted to these by means of a balljointed tube measuring approximately 4 by 18 mm which fitted onto the top of the flask just above its stopcock. The acid was run into the bulb slowly and the contents gently swirled to allow for complete absorption of hydrazine vapor by the liquid. After admission of air, aliquots were taken for dilution in 100 cc glass stoppered graduates, the final dilution to be in the range 0.001 to 0.006 mg hydrazine contained in 100 cc. Color was developed in the final dilution by making up to volume with water and 20 cc of "DAB" reagent, prepared with pure ethanol containing 10% hydrochloric acid and 2% p-dimethylaminobenzaldehyde. Light absorption was read in an electrophotometer after allowing ten minutes for color to completely develop.

A standard curve was prepared from known dilutions of hydrazine monosulfate in acid solution, assayed by potassium bromate titration at 50°C. In the range 0.001 to 0.008 mg hydrazine in 100 cc the solution absorption curve was linear when plotted logarithmically

against hydrazine concentration. Weekly checks of this curve with freshly prepared known dilutions of hydrazine failed to show at any time a deviation greater than 2%.

Some difficulties were encountered early in the work with the acid concentration of the final dilution which, if too high, had the effect of bleaching the color of the azine which is formed by the reaction of the benzaldehyde and the hydrazine. Measurements have shown that if more than 0.1 M of acid was present in the solution before the color reagent was added there was a significant decrease in light absorbency. Below that acid concentration no changes were observed. In all assays care was taken not to allow the acid concentration rise beyond the critical value.

In some cases the total hydrazine content of a sample was so low that a 50 to 80 cc aliquot was necessary for the photometric measurement. All samples were therefore dissolved in 0.1 M acid in order to keep them below the level at which the bleaching effect became apparent. It also seems indicated that in preparing the final dilution the "DAB" reagent, which is 0.1 M with respect to acid, should be added as the last step.

Mercury vapor and traces of copper were generally present in the gas sample. These act catalytically in the decomposition of hydrazine. In most cases the rate of decomposition of a synthetic sample added to the evacuated bulbs was found to be approximately 1 to 4% in 15 min, but occasionally values up to 7% were encountered. In order to minimize the decomposition the aliquots were treated with the color reagent as quickly as possible, generally within six minutes. The resulting azine compound was found to be stable up to 48 hrs. 10

The analytical method for the colorimetric determination of hydrazine was developed by W. A. James and sent to the project personnel by the Western Cartridge Company of East Alton, Illinois, in a personal communication in 1949. A later description of this same method is presented in Analytical Chemistry 24, 2006-8, 1952.

D. Computation of Experimental Results

Measurements obtained on the analytical train of the vacuum line provided two different quantities: (1) the mole fraction of noncondensable gases in the product, x_{nc} , (2) the mole fraction of hydrazine produced or destroyed in the discharge, $x_{N_2H_4}$.

Computations Involving Fundamental Data: To obtain the quantity x_{nc} the sample pressure p_s in the two liter flask "B", fig. 1, was first measured. After freezing out the condensable components the bulb was connected with one or both of the McLeod gages, each gage having a total volume of roughly 100 cc. The relative correction introduced by each of these additional volumes is roughly 5%. At the temperature of liquid nitrogen the cold finger of 15 cc volume contained an additional quantity of gas equivalent to $(300/78 - 1) 15 = 43$ cc, which represents an additional relative correction of 2%. The mole fraction of the noncondensable gases was thus computed from the equation

$$x_{nc} = a_i(p_{nc}/p_s) \quad (1)$$

where the factor a_i has the value 1.07 or 1.12 depending on whether one or both gages are in communication with flask "B", and where p_{nc} and p_s refer to the noncondensable and sample gas pressures defined in section 2A.

The hydrazine assay using flask "A" was reported in terms of grams of hydrazine in that bulb, denoted by the symbol, g . The molar quantity of hydrazine is thus $n = g/32$. The exact volume of each five liter bulb corresponds to 0.224 of the ideal molar gas volume at room temperature; hence the total number of moles of gas in the bulb is $N = 0.224(p_s/760)$, the pressure being given in mm Hg. The mole fraction of hydrazine in the sample was therefore computed as

$$x_{N_2H_4} = n/N = 106 (g/p_s) \quad (2)$$

Computations Involving Derived Quantities: In this section formulae are derived for computing the fraction of ammonia which is decomposed into hydrazine and into-noncondensable gases in the discharge. This establishes a common basis for intercomparison of all the runs regardless of operating conditions. For this purpose the stoichiometry for the decomposition of ammonia in the presence and absence of diluents must be examined.

Let

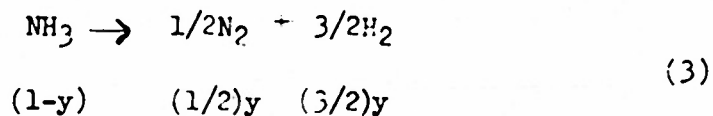
- a = moles H_2 mixed with one mole NH_3 .
- b = moles N_2 mixed with one mole NH_3 .
- x_0 = mole fraction non-condensable gases in reactant mixture.
- x_1 = mole fraction non-condensable gases in product.

x_2 = mole fraction hydrazine in product (chemical analysis)

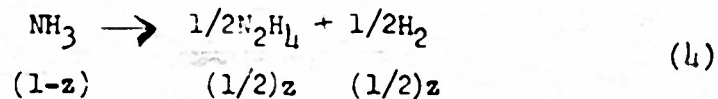
y = fraction of NH_3 decomposed into the elements.

z = fraction of NH_3 used to form hydrazine

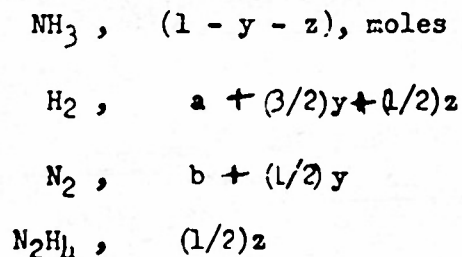
The reactions assumed are



and



The relative amounts of gases in the product are as follows:



Total Product = $(1 + a + b) + y$, moles

The mole fractions measured experimentally therefore are

$$x_0 = \frac{a+b}{1+a+b}; \quad (a+b) = x_0/(1-x_0) \quad (5)$$

$$x_1 = \frac{a+b + 2y + (1/2)z}{(1+a+b) + y} \quad (6)$$

$$x_2 = \frac{(1/2)z}{(1+a+b)+y} \quad (7)$$

Equation (6) and (7) are solved for y and then $(a+b)$ is replaced by means of equation (5):

$$y = \left(\frac{1}{1-x_0} \right) \frac{(x_1-x_2)-x_0}{2-(x_1-x_2)} \quad (8)$$

The fraction of ammonia used in hydrazine synthesis is then obtained from equation (7),

$$z = 2x_2 \left[\frac{1}{1-x_0} + y \right] \quad (9)$$

$$z = \frac{2x_2}{2-(x_1-x_2)} \cdot \frac{2+x_0}{1-x_0} \quad (10)$$

Several simplifications may now be introduced:

(a) For pure ammonia without any added gases $x_0=0$. Also, since in all runs $x_2 \ll x_1$ one finds

$$y \approx \frac{x_1}{2-x_1} \quad (11)$$

$$z \approx \frac{4x_2}{2-x_1} \quad (12)$$

(b) In the presence of added noncondensable gases where $x_2 \ll x_1$ one may effect the following simplifications

$$y = \frac{x_1 - x_0}{(1-x_0)(2-x_1)} \quad (13)$$

$$z = \frac{2x_2}{2-x_1} \quad \frac{2+x_0}{1-x_0} \quad (14)$$

(c) In some of the later computations the quantity x_1 in equation (14) was replaced by x_0 . This is permissible since the difference between these is very small. Under the least favorable circumstances the error introduced in this manner represents roughly 10% which is barely within the limits of experimental error in the hydrazine analyses. In most cases, however, the error introduced by this approximation was in the range of 3 to 5%.

Calculations of the power yield were carried out as follows:

Let F_n be the flow rate, in liters per minute, of ammonia through the reactor at room temperature and pressure. The flow rate in moles per hour is then given by $60 F_n/24.4$, the quantity in the denominator being the molar volume at room temperature. Let z be the fraction of ammonia decomposed into hydrazine on a molar basis. The quantity of hydrazine produced in grams per hour is therefore $z(60)(32) F_n/24.4$ (molecular weight of hydrazine is 32). Accordingly, the power yield is given by the relation

$$P = 79 z F_n / W_k \quad \text{in g/KWH}$$

where W_k is the power input in kilowatts.

Precision of Results Involving the Quantity y : The calculations for y according to equation (13) involves a large uncertainty due to the fact that the difference $x_1 - x_0$ in the majority of cases is quite small. This uncertainty is reflected in the scattering of the points in fig. 6.

It might be of interest to cite some numerical examples. The quantity x_1 or x_0 is proportional to the ratio p_{nc}/p_s . On the McLeod gage each of these pressure readings is determined by the product $p \sim h(h + H)$ where h and H are the positions of the mercury levels in the two capillaries relative to the tip of the closed capillary; both h and H are positive.

The absolute error in the level readings is assumed to be $\pm 0.5\text{mm}$. In a typical group of experiments (runs 73 to 77) the quantities h and H had values in the neighborhood of 180 and 270 mm respectively; the relative error in h is thus ± 0.003 and in $(h + H)$, ± 0.002 . The relative error in the pressure values can be shown to be approximately the sum of the individual relative errors, i.e. ± 0.005 . The maximum relative error in the ratio p_{nc}/p_s can likewise be shown to be approximately the sum of the two relative errors in p ; thus x_1 or x_0 is known with a precision of roughly 1%. In runs 73 to 77 the quantities x_1 and x_0 thus had an associated absolute error of ± 0.005 each, while the difference $x_1 - x_0$ was in the range 0.008 to 0.033. This shows that even under reasonably favorable conditions the relative error in y was of the order of 15 to 60%.

3. DECOMPOSITION OF AMMONIA

A. Pure Ammonia; Decomposition into Noncondensable Gases

The decomposition of pure ammonia into gases not condensable at liquid nitrogen temperature was examined over a wide range of conditions. The composition of the noncondensable gases was not determined. It could not deviate seriously from a 3:1 H₂: N₂ ratio, since the decomposition of ammonia into hydrazine plus hydrogen was always much less extensive than the total decomposition.

The results are presented in table 1. The quantity x_{nc} was originally plotted against W/F; however, these plots were omitted from the present report in favor of the more general graph, fig. 3. Here x_{nc} is the mole fraction of noncondensable gases in the product, W is the electric power in watts, and F is the flow in liters of gas per minute under room conditions of temperature and pressure. It will be noted that the ratio W/F is the energy supplied to unit amount of gas passing through the discharge. Examination of the x_{nc} vs. W/F graphs revealed the following interesting facts: (1) the plots were essentially independent of pressure; (2) at a given flow rate the plot of x_{nc} vs. W/F was quite linear; (3) the slopes of the linear plots were roughly proportional to the square root of F; (4) the intercepts of these plots all coincide.

If the observations (1) through (4) are valid, then all of the data of table 1 should fall on a single straight line when x_{nc} is plotted vs. W/\sqrt{F} . A graph of this type is shown in figs. 3a and 3b. Careful

examination of the points shows that these were scattered at random about the interpolated straight line: no systematic deviations pertaining to a given set of experimental conditions were detected. Thus, within a fairly large experimental error, the data can be represented in the analytic form

$$x_{nc} = 0.00074 W/F^{1/2} - 0.028 \quad (15)$$

W in watts

F in liters per min.

It appears from inspection of data lying below $W/\sqrt{F} = 60$ that the straight line eventually curves toward the origin. It should also be noted that the analytic expression given above is applicable to data which were obtained for flow rates ranging from one to ten liters per minute, over a pressure range from three to fifty millimeters of mercury, and that power inputs ranged from 50 to 675 watts. The decomposition of ammonia into noncondensable gases under the above experimental conditions can thus be neatly systematized.

B. Hydrazine Synthesis from Pure Ammonia

Data for the production of hydrazine from pure ammonia passing through the electric discharge are presented in tables 1 and 2, and are plotted in fig. 4 to 5.

As was discussed in section 2C, difficulties were encountered in the analytical determination of hydrazine. These were not caused by faulty analytical procedures as is indicated by the fact that known

Table 1. Conversion of Ammonia into Noncondensable Gases and into Hydrazine:
F, Flow rate; \bar{P} , average pressure prevailing in the discharge reactor; I, current; W, electrical power; x_{nc} , mole fraction of noncondensable gases; $x_{N_2H_4}$, mole fraction of hydrazine

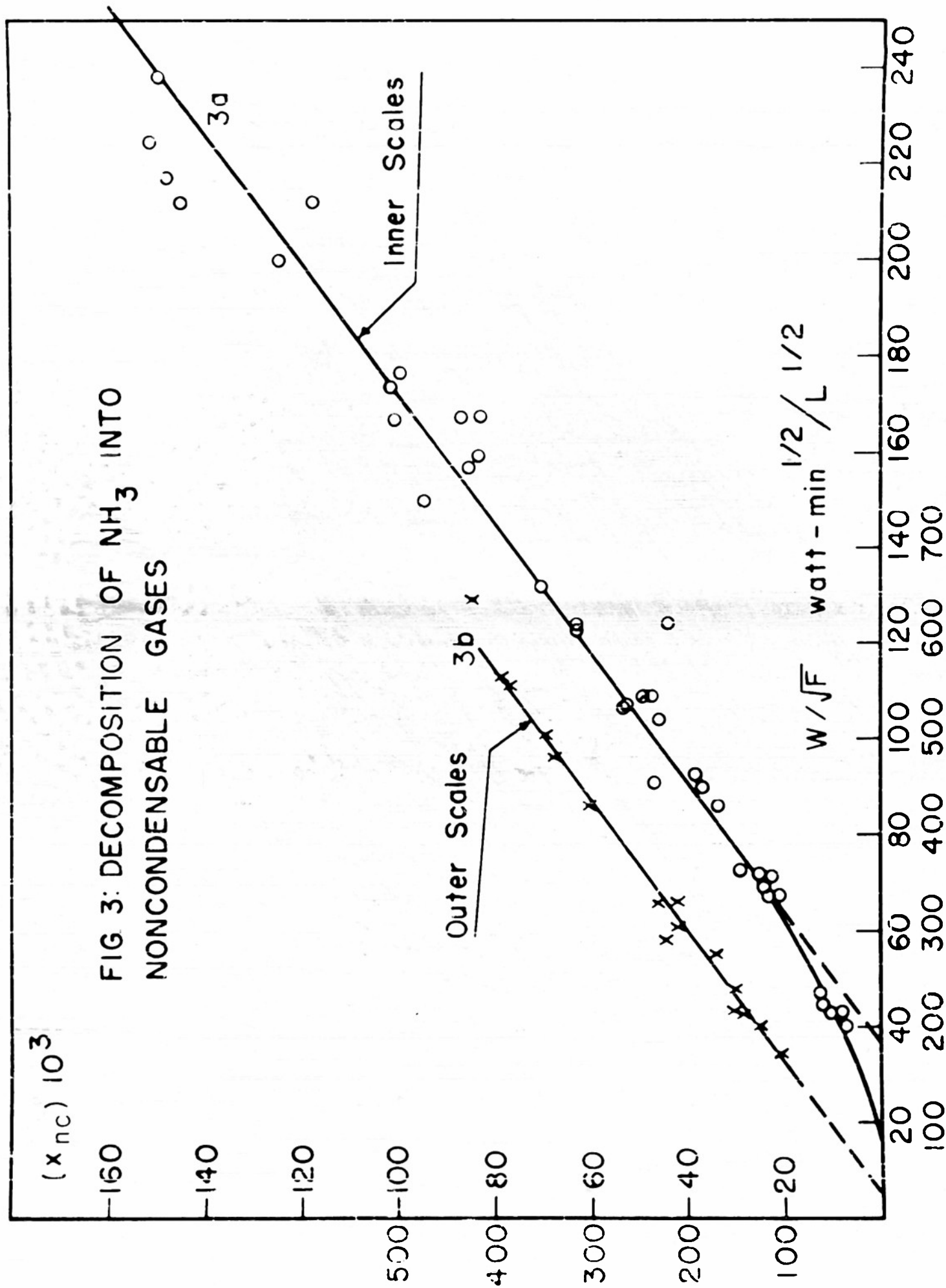
Run #	F l./min	\bar{P} mm Hg	I ma	W Watts	$x_{nc} \times 10^3$	$x_{N_2H_4} \times 10^3$
8	4.8	10	106	370	12.5	1.61
9			65.7	238	23.8	1.69
10			41	156	52.5	1.95
11			26	105	87.0	1.79
13		15	45.4	190	34.1	2.10
14			69.5	274	62.6	2.56
15			106	392	100.	2.40
16			37.0	159	24.5	1.94
17		23	40	202	46.7	2.29
18			70	332	95.0	2.09
19			110	474	-	1.83
20			112	480	148	1.81
22	9.7	18	40.8	210	21	1.5
26			42	210	23	1.6
23			65	340	49	1.5
24			105	500	84	1.6
25			107	490	86	1.6
42		25	50.5	290	39	1.9
43			75	410	70	2.2
44			105	540	103	2.1
35	2.4	5	19.8	62	10	2.7
37			20.7	67	10	2.7
38			35	110	23	2.5
39			65	190	63	2.7
40			106	310	125	2.4
27		15	33	140	37	2.7
28			46.5	180	56	2.4
29			71.0	260	101	2.5
30			108	370	150	2.1

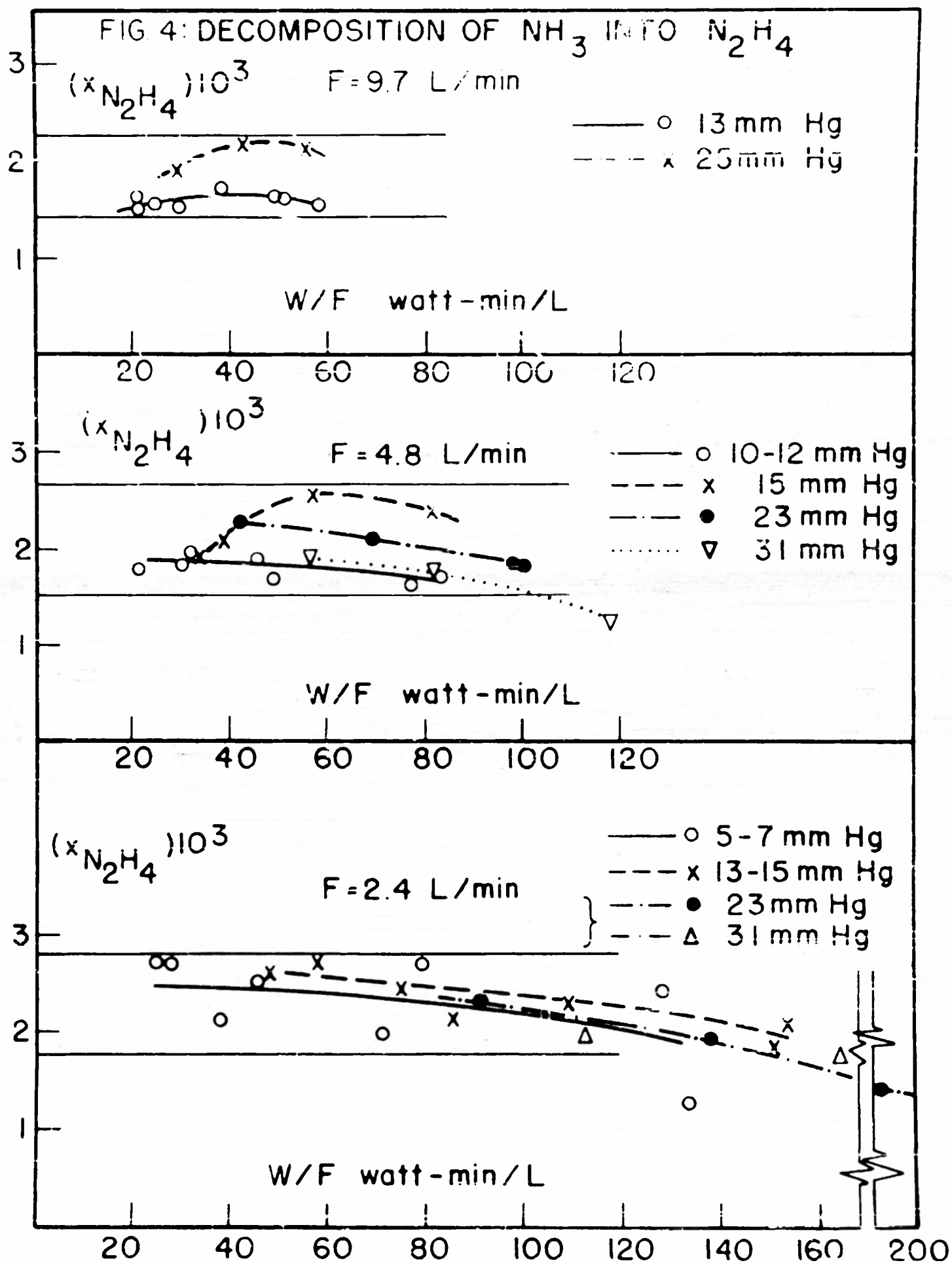
Table 1. (continued)

Run #	F L/min	\bar{p} mm Hg	I ma	W Watts	$x_{nc} \times 10^3$	$x_{N_2H_4} \times 10^3$
34		23	46	220	96	2.3
33			73	330	145	1.9
31			117	470	212	1.4
54	1.07	40	91	469	(371)	.87
49			105	500	344	.86
52			99.3	525	348	.71
51			118	587	392	.69
50		50	108	673	424	.32
56		30	73	345	229	1.2
55			122	546	388	.78
48		20	50	234	151	2.4
58			76	304	221	1.7
57			119	450	304	1.2
61		10	29	108	46	3.3
60			71	220	118	2.6
59			117	347	207	2.1
62		3	18.3	46	14	
63			30	76	29	
64			45.5	112	47	
65			70.0	174	83	
66			116	288	168	

Table 2: Conversion of Ammonia Into Hydrazine. Symbols Have Same Significance as in Table 1.

Run #	F l./min	P mm Hg	I ma	W Watts	$x_{N_2H_4} \times 10^3$
95	2.4	7	29.7	91.5	2.12
96			59.9	171	1.29
97			115	322	1.26
98		13	30.0	114.5	2.59
99			61.0	206	2.21
100			116	365	1.74
101		31	45	224	1.76
102			67	344	1.50
103			119	546	1.04
104	4.8	12	30.5	121	1.81
105			60.2	221	1.87
106			115	401	1.69
107		31	45	270	1.89
108			74	396	1.71
109			118	566	1.22
110	9.8	19	45	235	1.55
111			72	373	1.70
112			115	565	1.52
130	1.07	3.5	13	-	6.16
131			29.8	73.0	3.34
132			51.0	124	3.64
133			75.4	183	3.74
134			100.3	241	3.54
135			122	294	(1.01)
136			12.8	31.2	3.26
137		10	16.8	66	3.25
138			32.0	110	2.77
139			49.5	158	2.50
140			81.5	243	2.67
141			121	351	1.83





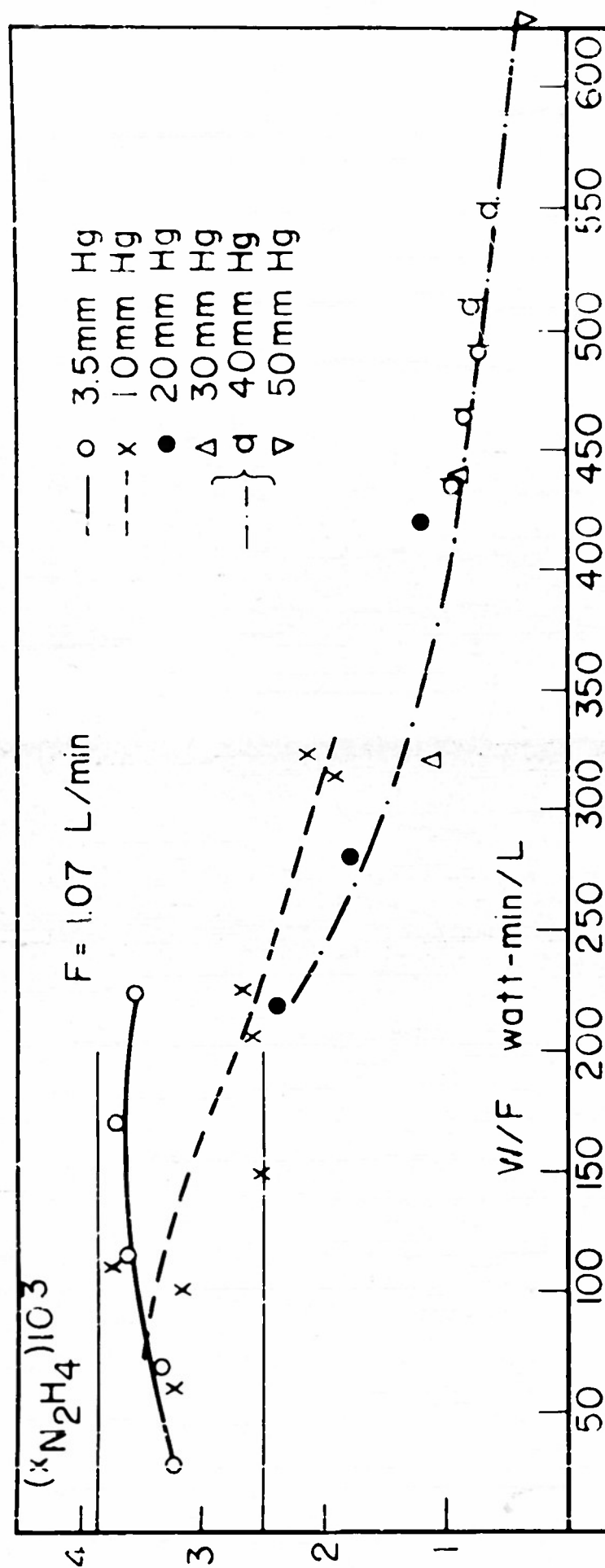


FIG. 5: DECOMPOSITION OF NH_3 INTO N_2H_4

solutions of hydrazine, prepared as a check against the procedures, were always assayed correctly. The fact that the hydrazine assays of the experimental samples show severe scattering is taken as an indication that the conditions under which these experiments were run could not be controlled sufficiently to allow for reproducible assays. No attempts were made to subject the operating condition specified in section 2A to more stringent controls.

Despite the scattering of the data several features common to these curves can be characterized: (1) At low values of W/F (for definition of symbols refer to section 3A; W given in watts, F in liters per minute) in the range $20 < W/F < 160$ the hydrazine yields seem to be little affected by the power input; the yields in this range of W/F all lie between two limiting values indicated by the horizontal lines in fig. 4 to 5. (2) In the range $20 < W/F < 160$ the average quantity of hydrazine in mole percent in the discharge products decreases slightly as the flow rate increases. These values are listed below in table 3.

Table 3. Average Values for Mole Fraction of Hydrazine Produced from Pure Ammonia as a Function of Flow Rates in the Range $20 < W/F < 160$ watt-min/L

Flow rate(L/min)	9.7	4.8	2.4	1.07
$x_{N_2H_4}$	1.8	2.1	2.4	3.2

(3) Beyond $W/F = 160$ the hydrazine yield decreases rapidly with increasing power output. In fig. 5 (flow rate of 1.07 L/min) the drop in hydrazine yield with increasing W is fairly sharp in the range

$200 < W/F < 350$; beyond this range there is little further change in $x_{N_2H_4}$ with W/F . (4) As a first approximation, variations in pressure at a constant flow rate have relatively little effect on the variation of $x_{N_2H_4}$ with W/F . Careful examination of the data shows that with increasing pressure the hydrazine yield decreases somewhat.

The above results will be discussed further, together with other experimental work in section 5. A few remarks of a more general nature are appended here: (5) It is clear that at $W/F = 0$, $x_{N_2H_4} = 0$. Consequently, all plots of $x_{N_2H_4}$ vs. W/F must start at the origin and pass through a maximum in the range $20 < W/F < 160$, before decreasing again. For $W/F = 60$ relatively flat maxima are actually observable in a number of favorable cases (see runs at 4.9 L/min). However, because of the scattering of the data these maxima are not well defined; since further, the region $W/F < 20$ was inaccessible experimentally, it seemed justified to characterize the data in the range $20 < W/F < 160$ by observation (1). (6) It is to be noted that at best the mol fraction of hydrazine present does not exceed 4×10^{-3} . This value, equivalent to 0.8g hydrazine in 100g ammonia, is in line with those obtained over a period of 45 years by different investigators, and with experimental data obtained with large scale reactors earlier on this project. (7) In the range $W/F < 160$ and at a constant flow rate, $x_{N_2H_4}$ is roughly independent of W , and x_{nc} increases linearly with W . Thus, in order to minimize the decomposition of ammonia into the elements nitrogen and hydrogen relative to the decomposition into hydrazine, the lowest power inputs capable of sustaining the discharge should be employed. If the power input is such

that $W/F > 150$ then the relative $N_2H_4/(N_2 + H_2)$ yield diminishes even more rapidly. Under favorable conditions the ratio of moles of noncondensable gases to moles of hydrazine obtained in the ammonia decomposition was of the order of 3 to 4. In most cases this ratio was of the order of 40 while under conditions of high power input the ratio was as high as 1000. Thus, as far as production of hydrazine is concerned, the use of an electric discharge under the conditions described earlier yields mostly unwanted by-products. (8) Calculations concerning the power yields showed that these ranged from 0.04 to 8 g hydrazine per kilowatt-hour. These values again are in line with those cited by other workers and found earlier on this project. As the flow rate is decreased under constant electrical conditions the power yield is found to pass through a maximum. At a given flow rate the most favorable power yields are obtained at the lowest possible power inputs. An increase in the reactor gas pressure decreases the power yield slightly.

C. Decomposition of Ammonia in the Presence of Water Vapor

Experimental results concerning the decomposition of ammonia in the presence of small quantities of water vapor are presented in Table 4. The mole fraction of noncondensable gases produced in the electric discharge under various conditions is listed under the column x_{nc} . The comparable values obtained in the absence of water vapor are listed under the column x_{nc}^0 ; these values were read from the graph presented in fig. 3, pertaining to dry ammonia.

It is apparent upon comparing these two columns in table 4 that the addition of water in mole fractions from 0.018 to 0.043 produces no pronounced effect on the total decomposition of ammonia under the conditions studied. The differences in these figures are no greater than corresponding deviations of the data upon which the plot in fig. 3 is based.

The conversion of ammonia into hydrazine in the presence of the water vapor is also listed in table 4. Comparison of these values with fig. 4 or 5 shows that in every case the mole fraction of hydrazine is only half as large as that obtained under comparable conditions with pure, dry ammonia. More exact intercomparisons are not possible, due to the scattering of the data.

It is concluded that the addition of small quantities of water vapor to ammonia does not affect the extent of total decomposition of ammonia into the elements. The already small conversion into hydrazine is halved, however, in the presence of these small quantities of water vapor.

D. Ammonia Decomposition in the Presence of Nitrogen and Hydrogen

General Discussion: The decomposition of ammonia-nitrogen or ammonia-hydrogen mixtures in an electric discharge is of practical interest since the decomposition of pure ammonia results principally in the formation of nitrogen and hydrogen. In an recycle manufacturing process the concentration of these noncondensable gases would increase greatly in successive stages.

Table 4: Decomposition of Ammonia in the Presence of Water Vapor: Flow rate of water vapor 0.086 L/min (NTP). F, flow rate of ammonia; \bar{P} , average gas pressure in the reactor; I, discharge current; W, power input; x_{nc} and x_{nc}^o , mole fraction of noncondensable gas produced in the presence and absence of water vapor respectively; $x_{N_2H_4}$, mole fractions of hydrazine produced in the presence of water vapor; x_{H_2O} , mole fraction of water present in ammonia.

Expt. #	F L/min	P mm Hg	I ma	W Watts	$(x_{nc})10^3$	$(x_{nc}^o)10^3$	$(x_{N_2H_4})10^3$	$x_{H_2O}^o$
89	4.8	10	100	360	79.0	93	0.84	0.018
90			90	201	45.5	13	1.83	
91			30	130	20.5	19	1.74	
94		33	117	585	187	176	1.19	
99	2.0	6	117	308	120	130	0.72	0.043
90			60	163	50.5	58	1.19	
91			30	91	23.0	22	2.51	
92		12	117	355	164	170	1.59	
93		30	117	538	267	262	1.07	

Under operating conditions favorable to the formation of hydrazine from pure ammonia, hydrogen and nitrogen are produced in concentrations of the order of 5 to 20 mole percent in the product mixture. No new effects could therefore be anticipated by the admixture of noncondensable gases at an initial concentration of 20 mol percent. Consequently, a 50:50 starting mixture of ammonia with nitrogen or hydrogen was used.

Decomposition of Ammonia into Noncondensable Gases: The experimental data obtained with ammonia-nitrogen or ammonia-hydrogen mixtures are presented in tables 5 and 6. The various values of x , y , z , were calculated as explained in detail in section 2 D.

Fig. 6, curve (a), represents the fraction of the ammonia in the starting mixture which has been decomposed into noncondensable gases, y , as a function of W/\sqrt{F} . As discussed in section 2 D, the scattering of the experimental points in this graph is a consequence of the calculations in formula (14). These calculations involve small differences between nearly equal numerical values.

It is seen nevertheless, that the majority of the experimental points lies well below the straight line (b) which plots y versus W/\sqrt{F} when pure ammonia was passed through the discharge. Curve (b) was obtained from fig. 3, using formula (11). It is to be concluded that when nitrogen or hydrogen are initially admixed with ammonia, the fractional decomposition of 2NH_3 into $\text{N}_2 + 3\text{H}_2$ is considerably

Table 5: Decomposition of Ammonia-Nitrogen Mixtures: F, flow rate; \bar{P} , average gas pressure in reactor; I, discharge current; W, power input; x_0 , mole fraction of N_2 present in starting mixture; x_1 , mole fraction of noncondensable gas present in effluent gas; x_2 , mole fraction of hydrazine present in effluent mixture; y, z, fraction of ammonia in starting mixture which has been converted to noncondensable gases and to hydrazine respectively.

Expt. #	F L/min	P mm	I ma	W Watts	$(x_0)10^3$	$(x_1)10^3$	$(x_2)10^3$	$(y)10^3$	$(z)10^3$
147	1.8	12	30.5	112	468	472	0.87	5	5.4
146			59	200	475	469	0.71	-	4.4
145			116	382	482	494	0.70	15	4.4
202	2.1	8	14.5	43.4	505		0.504		3.5*
151			15.5	49.0	560		0.500		3.3*
201			31.0	87.7	535		0.535		3.7*
150			30.5	39.0	455	461	0.850	7.0	5.00
200			48.2	132	505		0.838		5.7*
149			59.0	164	462	465	0.301	3.6	1.80
199			70.7	194	492		0.354		2.3*
198			88.5	251	492		0.313		2.1*
197			110	306	492		0.402		2.7*
148			116	327	450	494	0.363	53	2.11

* Approximate Calculation as described in section 2D.

Table 6: Decomposition of Ammonia-Hydrogen Mixtures: For definition of Symbols see table 5, except that x_0 refers to mole fraction of hydrogen present in starting mixture.

Expt. #	F l/min	P mm	I ra	W Watts	$(x_0)10^3$	$(x_1)10^3$	$(x_2)10^3$	$(y)10^3$	$(z)10^3$
95	5.6	11	30	122	114	125	1.58	6.6	4.0
94			65	240	117	152	1.37	21	3.6
63			66	251	533	563	0.31	0	2.7
83			115	102	116	135	0.90	44	2.4
193	4.8	10	12.3	48.2	498		0.500		3.3*
71			23.0	88.2	538	538	0.67	0	5.1
192			31.9	119	498		0.876		5.3*
191			50.3	185	498		0.855		5.7*
72			56.3	204		540	0.79		5.8*
80			56.8	205	522	531	1.17	13	8.3
190			67.1	241	551	498	1.05	26.6	7.22
189			89.0	324	550	503	0.867	17.3	6.04
188			112	410	560	496	0.675	57.8	4.57
77	2.1	4	7.3	20		488	0.35		2.2*
76			12	32		492	0.52		3.4*
75			25	69	490	499	1.06	12	6.9
194			40.0	114	510		1.35		10 *
74			51	154	496	516	1.70	27	11.3
195			65.5	193	510		1.54		12 *
196			89.3	262	510		0.954		7.3*
76	2.1	10	101	367	481	526	0.57	59	3.7
79		16	100	405	503	537	0.65	47	4.4
82		31	100	510	542	545	0.42	45	3.2

* Approximate calculation as described in section 2D.

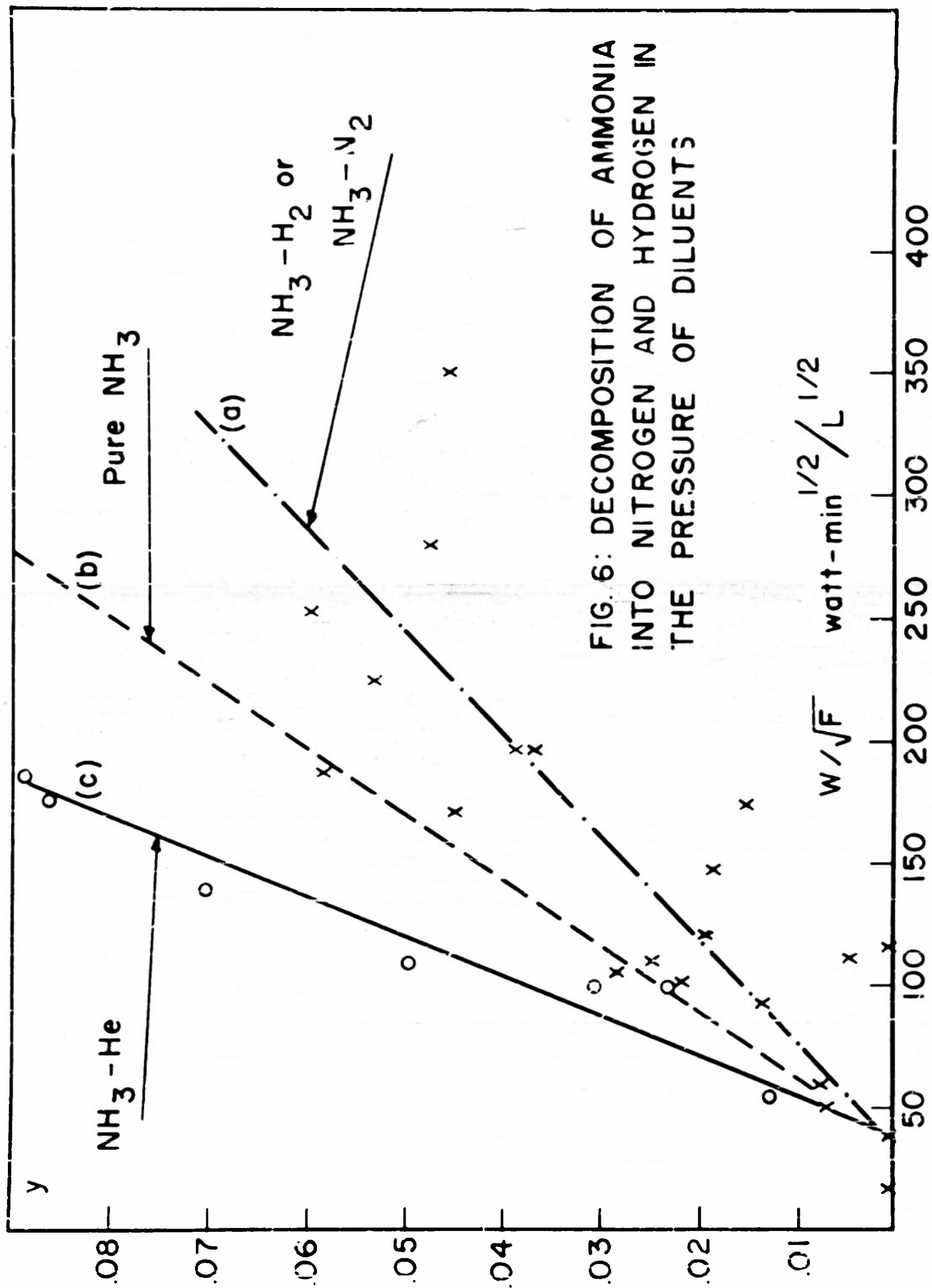


FIG. 6: DECOMPOSITION OF AMMONIA INTO NITROGEN AND HYDROGEN IN THE PRESENCE OF DILUENTS

decreased. The scattering of the data does not permit any comparison to be made between the effectiveness of nitrogen and hydrogen in suppressing this relative decomposition. Similarly, it is not possible to decide whether, as in the case of pure ammonia, the plot of y versus W/\sqrt{F} yields a straight line.

Decomposition of Ammonia into Hydrazine: The fraction of ammonia present in the starting mixture which is decomposed into hydrazine is listed in tables 5 and 6. This quantity z is plotted against W/F in figs. 7 and 8. For comparison the range of z values obtained with pure ammonia is shown as horizontal dotted lines. These z values were calculated from figs. 4 and 5 using equation (12).

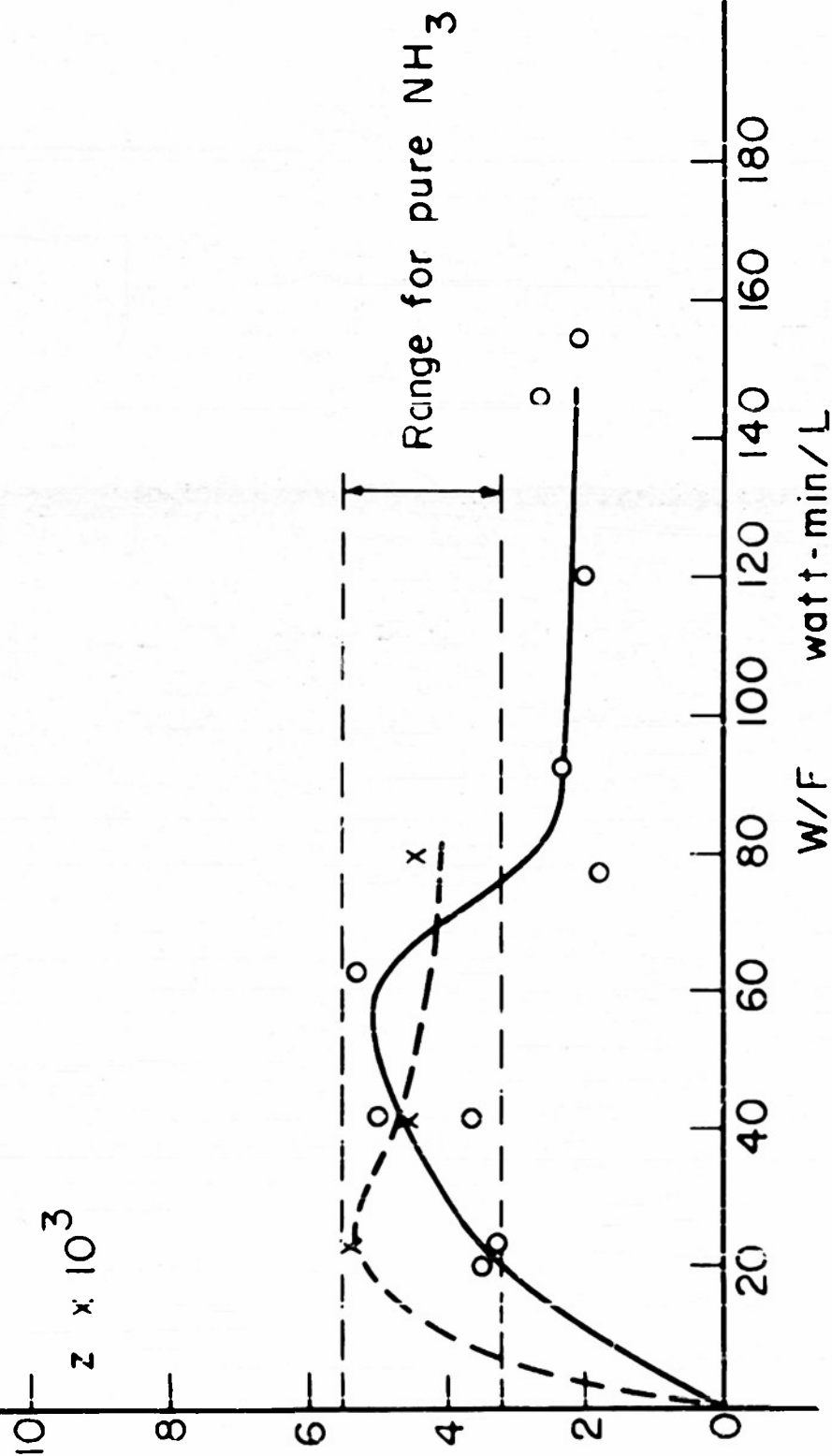
Inspection of these figures shows the following: (a) When nitrogen is used as a diluent the fraction of ammonia decomposing into hydrazine never exceeds that observed with pure ammonia. For $W/F > 80$ this value z is even considerably less for the ammonia - nitrogen mixture than for ammonia itself. Compared to the curves in figs. 4 or 5 (pure ammonia), the plots in fig. 7 show a much more pronounced maximum. It can be concluded that the presence of nitrogen in the discharge is detrimental to the formation of hydrazine.

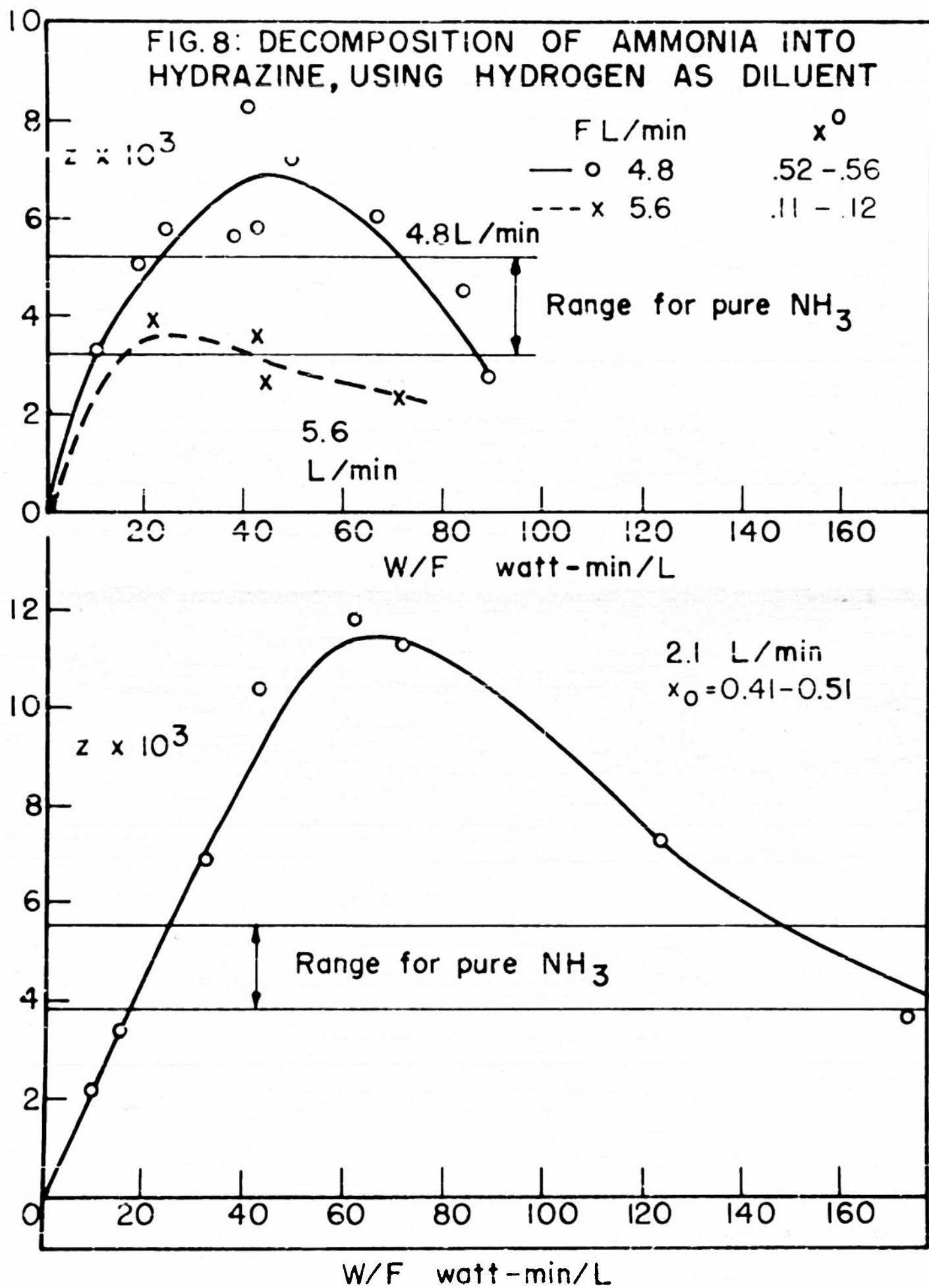
(b) When hydrogen is used in the starting mixture the fraction z at medium power inputs is greater in the presence than in the absence of this diluent at low flow rates. As the power input is raised at a given flow rate the quantity z passes through a maximum which is very pronounced at low flow rates. As the flow rate is increased the position of the

FIG. 7: DECOMPOSITION OF AMMONIA INTO HYDRAZINE IN
THE PRESSURE OF NITROGEN AS DILUENT

$$x_0 = 0.45 - 0.48$$

x 4.8 L/min
o 2.1 L/min





maximum shifts toward the origin and decreases in size. Under appropriate conditions, a two to three fold increase in z was obtained over that corresponding to pure ammonia.

Since the presence of hydrogen not only inhibits the decomposition of ammonia into noncondensable gases but also increases the conversion of ammonia into hydrazine its usefulness as an additive should be further investigated.

Power yields obtained with hydrogen as diluent were found to decrease from 9.4 to 2.3 g/KWH as power input was raised from minimal to maximal values at flow rate of 2.1 L/min. At a flow rate of 4.8 L/min the power yields decreased from 13 to 2.1 g/KWH. These values are more favorable than those obtained with pure ammonia under comparable conditions. The power yields decrease uniformly as z passes through its maximum with increasing power input. Consequently, best power yields always obtain at the lowest power levels which will barely sustain the discharge, but not at the levels required for obtaining maximal z values.

The maximal value $z = 12 (10^{-3})$, observed in run 195, corresponds to the low conversion of 1.2 g hydrazine per 100 g ammonia. This value is larger by a factor of three halves than the comparable value obtained with pure ammonia.

E. Ammonia Decomposition in the Presence of Helium

It seemed of interest, in view of the results obtained with hydrogen, to examine the effect of helium as a diluent. Accordingly, 60 - 40 or 90 - 10 mixtures of ammonia and helium were passed through the electric discharge under a variety of conditions. The results are presented below.

Decomposition of Ammonia into Nitrogen and Hydrogen: The fraction y of ammonia which is decomposed into noncondensable gases under specified conditions is listed in table 7. A plot of y vs. W/\sqrt{F} is shown in fig. 6, curve (c). Comparison to the curve obtained with pure ammonia shows that the decomposition is enhanced in the presence of helium. As in the case of pure ammonia, the data on this plot fall on a straight line.

Decomposition of Ammonia into Hydrazine: Data on the conversion of ammonia into hydrazine are given in table 7. The quantity z is plotted against W/F in figs. 9 and 10. Inspection of these graphs shows the following: (a) The z values pass through a very sharp maximum as the power input is increased. (b) The position of the maximum is shifted toward the origin and is accentuated as the flow rate is raised. In these two respects the behavior of helium as a diluent is the same as that of hydrogen. (c) Compared to the experiments carried out with pure ammonia, the fractional conversion of ammonia into hydrazine, z is increased by a factor of two to three. The highest z values of the order of 17×10^{-3} were found in the run carried out at a flow rate of 1.1 L/min; this value represents a conversion of 3.4 g hydrazine produced per 100 g ammonia introduced to the discharge. The extent of conversion thus is still quite

Table 7: Decomposition of Ammonia in Electric Discharges, using helium as diluent; F, flow rate; \bar{P} , average pressure in discharge tube; I, discharge current; W, power input; x^0 mole fraction of helium gas used in the starting mixture; x_1 , mole fraction of noncondensable gases in the product mixture; x_2 , mole fraction of hydrazine in product mixture; y and z, fraction of ammonia, initially present in starting mixture, which has been decomposed into noncondensable gases and into hydrazine respectively. Last two quantities computed on a molar basis.

Expt. #	F L/min	P mm Hg	I ma	W Watts	$(x_0)10^3$	$(x_1)10^3$	$(x_2)10^3$	(y) 10^3	(z) 10^3
166	3.4	7	11	36	394		1.21		6.0*
165			20.7	64.3	394		1.47		7.3*
164			32.2	102	386	398	3.02	12	14.5
167			60	185	376	398	2.91	22	13.9
170			60	186	374	404	2.27	30	10.9
163			66	204	384	432	2.60	49	12.8
168			85	255		442	1.36	70	6.6**
171			113	339	368	452	0.94	86	4.6
169			115	345		460	0.97	88	4.3**
203	2.1	8	11.1	32.3	365		1.63		7.4***
204			29.1	83.5			3.23		14.7
205			49.8	141			2.34		10.6
206			68.4	193	422		1.90		10.1
207			90.0	246			1.42		7.5
208			108	290			1.04		5.5
210			24.5	69.1	389		2.31		11.2
211			34.7	101			2.95		14.5
212			45.7	131			3.44		16.8

*Approximate calculation as described in section 2D.

**Estimated, taking $x_0 = .27 \pm .01$ by analogy to run 167 done at the same time.
Error in z introduced is roughly 5%.

***All results in this column calculated as shown in section 2D.

Table 7 (Continued)

Expt #	F L/min	\bar{P} mm Hg	I ma	W Watts	$(x_3)10^3$	$(x_1)10^3$	$(x_2)10^3$	$(y)10^3$	$(z)10^3$
213	1.1	6	26.1	71.0	{ 380		3.22		15.3 ***
214			35.9	96.0			3.65		17.3
215			46.9	122			3.60		17.0
216			56.2	148	{ 379		2.30		10.9
217			75.4	192			1.45		6.87
218			99.8	244			1.17		5.54
219		31	35.2	172	{ 366		1.03		5.33
220			50.4	247			1.16		3.87
221			65.7	306			.843		5.44
225	2.1	8	15.3	48.4	{ 74.7		1.65		3.01
226			23.5	70.5			1.75		4.04
222			34.5	104	{ 69.5		2.35		5.44
223			50.5	145			1.75		4.02
224			62.8	181			1.83		4.23
227			90.9	260	{ 74.7		1.42		3.28

***All results in this column calculated as shown in section 2D.

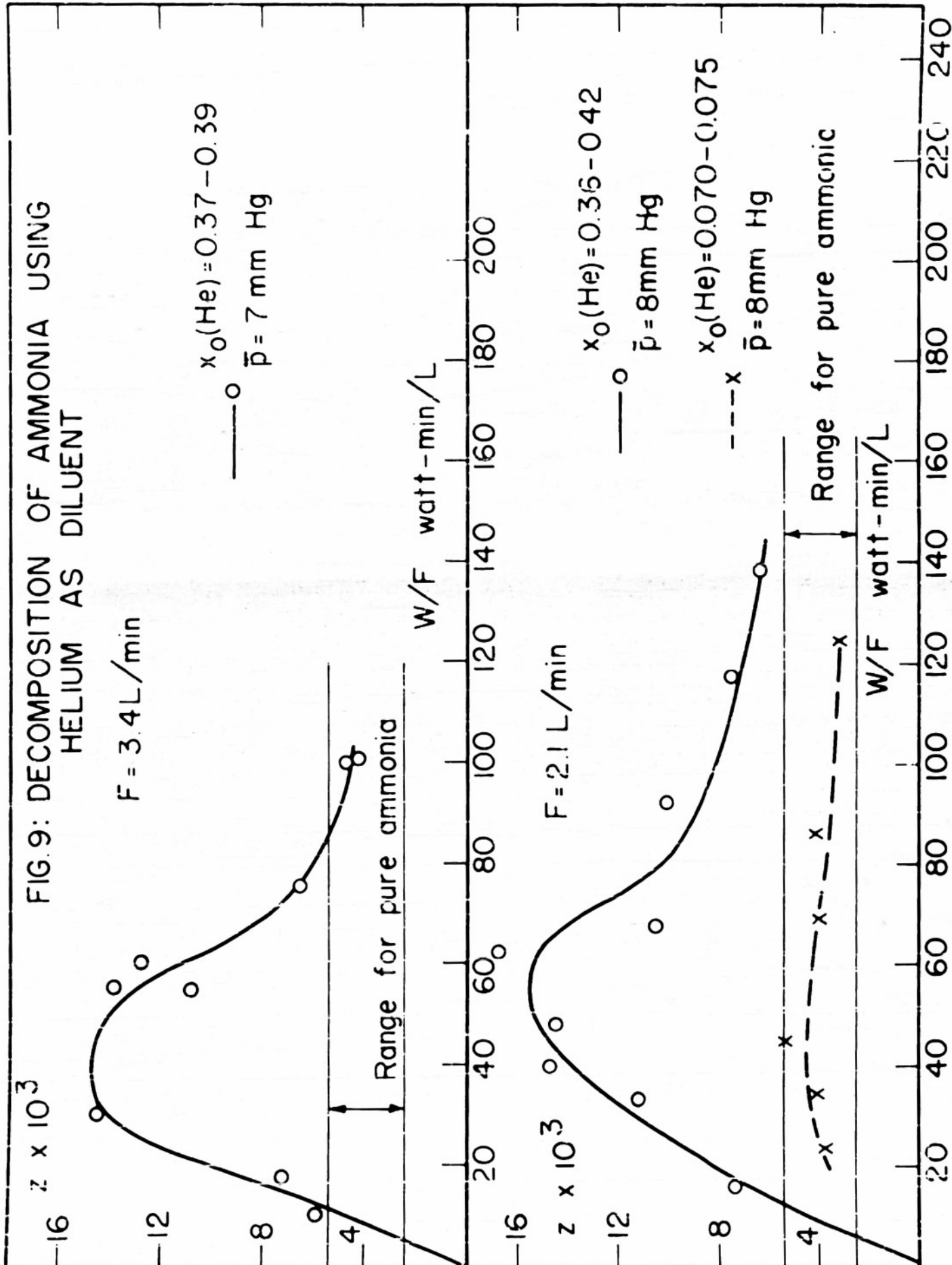
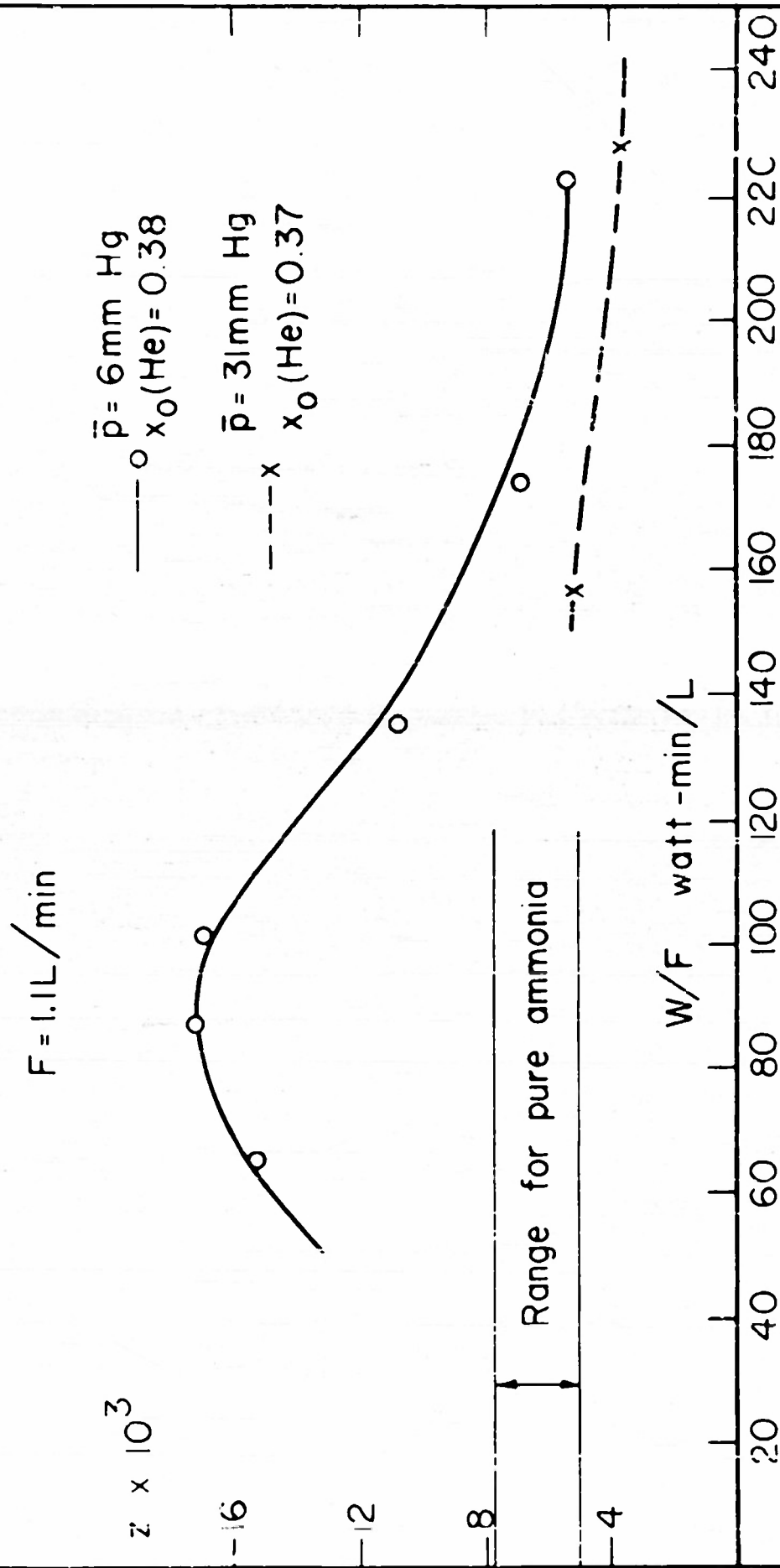


FIG 10: DECOMPOSITION OF AMMONIA USING
HELIUM AS DILUENT



small. (d) In one set of runs the ratio of helium to ammonia introduced to the reactor was of the order of 7 to 8 mole percent. The data are plotted in fig. 9. The results very closely resemble those obtained with pure ammonia. Thus the presence of helium as diluent in low proportions does not affect the extent of decomposition of ammonia into hydrazine.

Power yield calculations for a variety of experimental conditions are presented in table 8.

Table 8. Power Yields Obtained in the Decomposition of Ammonia into Hydrazine, Using Helium as Diluent; F, flow rate; x_0 mole fraction of ammonia in starting mixture; P_1 , maximum power yield; P_2 , minimum power yield.

F L/min	x_0	P_1 g/kwh	P_2 g/kwh
3.4	0.37 to 0.39	22.3	1.63
2.1	0.36 to 0.42	21.3	1.55
2.1	0.070 to 0.075	12.3	2.0
1.1	0.37 to 0.38	9.3	0.68

Since these power yields decrease monotonically as the power input is raised it is found, as in the case where hydrogen is used as diluent, that optimum power yields occur at the lowest possible power inputs. Therefore, in the range of higher power input where z attains its maximum the power yield is notably poorer. Under optimum conditions the power yields attained in these experiments are three times as large as those obtained with pure ammonia. In the range of power input where z reaches its maximum the power yields are up to twice as large as the

best yields obtained with pure ammonia. Even for helium admixtures in the range of 7 mole percent the power yields are markedly improved over those obtained with pure ammonia under identical conditions.

Since the use of helium as a diluent increases the power yields considerably the conversion of ammonia to hydrazine in the presence of this additive merits further study.

4. DECOMPOSITION OF HYDRAZINE IN DISCHARGES, USING AMMONIA, NITROGEN, HYDROGEN, OR HELIUM AS CARRIER GASES

A. Introduction

The premise that hydrazine decomposes rapidly in an electric discharge has been advanced repeatedly and is often used as a basis for attempts to improve hydrazine yields in ammonia conversion. It is therefore of great importance to ascertain how readily hydrazine is destroyed under the action of the discharge plasma. For this purpose hydrazine was admixed with carrier gases; the mixture was then passed through the discharge and the hydrazine concentration was determined before and after passage through the reactor.

B. Decomposition as a Function of Power Input

The decomposition of hydrazine as a function of power input in the discharge was studied using ammonia, nitrogen, hydrogen, and helium as carrier gases. Results are reported in tables 9A to 9D and in figs. 11 and 12. In these figures the ratio X/X_0 is plotted against W/F .

Table 9: Decomposition of Hydrazine in an Electric Discharge, Using Various Carrier Gases: F, flow rate; \bar{P} , gas pressure in reactor; I, discharge current; W, power input; X_0 and X , mole fraction of hydrazine present initially and in the effluent gas mixture respectively; x_{nc} and x_{nc}^0 mole fraction of noncondensable gases present in the product mixture, when ammonia in the presence or absence of hydrazine is passed through the discharge.

Expt. #	F L/min	\bar{P} mm Hg	I ma	W Watts	$(X)10^3$	$(X_0)10^3$	X	$(x_{nc})10^3$	$(x_{nc}^0)10^3$
(A) AMMONIA - HYDRAZINE									
113	4.80	12	30	120	4.14	5.05	0.82	16.8	16.2
114			61	230	2.91	4.96	0.59	46.4	51
115			116	405	2.06	5.05	0.41	107	112
119	1.07	5	17	55	12.1	21.2	0.57	31.7	16
116			30	87	9.11	19.8	0.46	46.7	37
117			61	160	3.86	20.8	0.19	93	93
118			121	326	2.54	19.7	0.13	217	220
121		16	33	136	3.44	20.4	0.17	94.4	75
122			64	235	2.99	19.1	0.15	148	150
120			122	402	2.59	21.6	0.12	263	280
(B) NITROGEN - HYDRAZINE									
172	1.07	6	18.1	63.3	24.6	42.5	0.578		
173			34.9	106	15.0		0.353		
174			55.1	153	0.713	45.3	0.0157		
175			75.3	211	0.127		0.00280		
176			89.4	252	0.0702	43.1	0.00163		
177			117	322	0.0483		0.00112		

*read off from fig. 3.

Table 9. (Continued)

Expt #	\bar{P} L/min mm Hg	\bar{I} ma	\bar{W} Watts	$(X)10^3$	$X_0 10^3$	X/X_0
178	4.8	15	230	1.46	8.28	0.177
179		56.6	280	0.532		0.0640
180		72.7	342	0.0985	7.70	0.0128
181		89.7	406	0.0817		0.0107
182	2.4	8	105	8.30	18.2	0.456
183		37.0	148	5.22		0.286
184		50.1	193	0.766	18.6	0.0412
185		62.4	236	0.236		0.0127
186		74.3	275	0.106	15.7	0.00673
187		91.3	331	0.0152		0.00097
(C) HYDROGEN- HYDRAZINE						
127	1.07	6	22	14.7	23.0	0.64
126		16	49	8.2	20.8	0.39
125		31	92	0.92	20.6	0.046
123		60	196	0.51	22.0	0.023
123		122	368	0.55	20.8	0.026
(D) HELIUM- HYDRAZINE						
153	4.8	7	6.0	2.32	2.73	0.85
154		15.2	19.0	1.75		
155		31.0	40.0	0.63	3.62	0.175
156		51.4	70.5	0.085	2.96	0.039
157		78.8	112	0.049	2.96	0.017
152		118	175	<0.04	2.32	<0.017
158	2.4	6	7.6	6.10	11.2	0.545
159		14.7	18.1	4.62	11.2	0.414
160		30.5	39.0	0.23	9.13	0.025
161		60.7	85.0	0.11	9.13	0.012

FIG. II: DECOMPOSITION OF HYDRAZINE
USING AMMONIA OR NITROGEN AS
CARRIER GASES

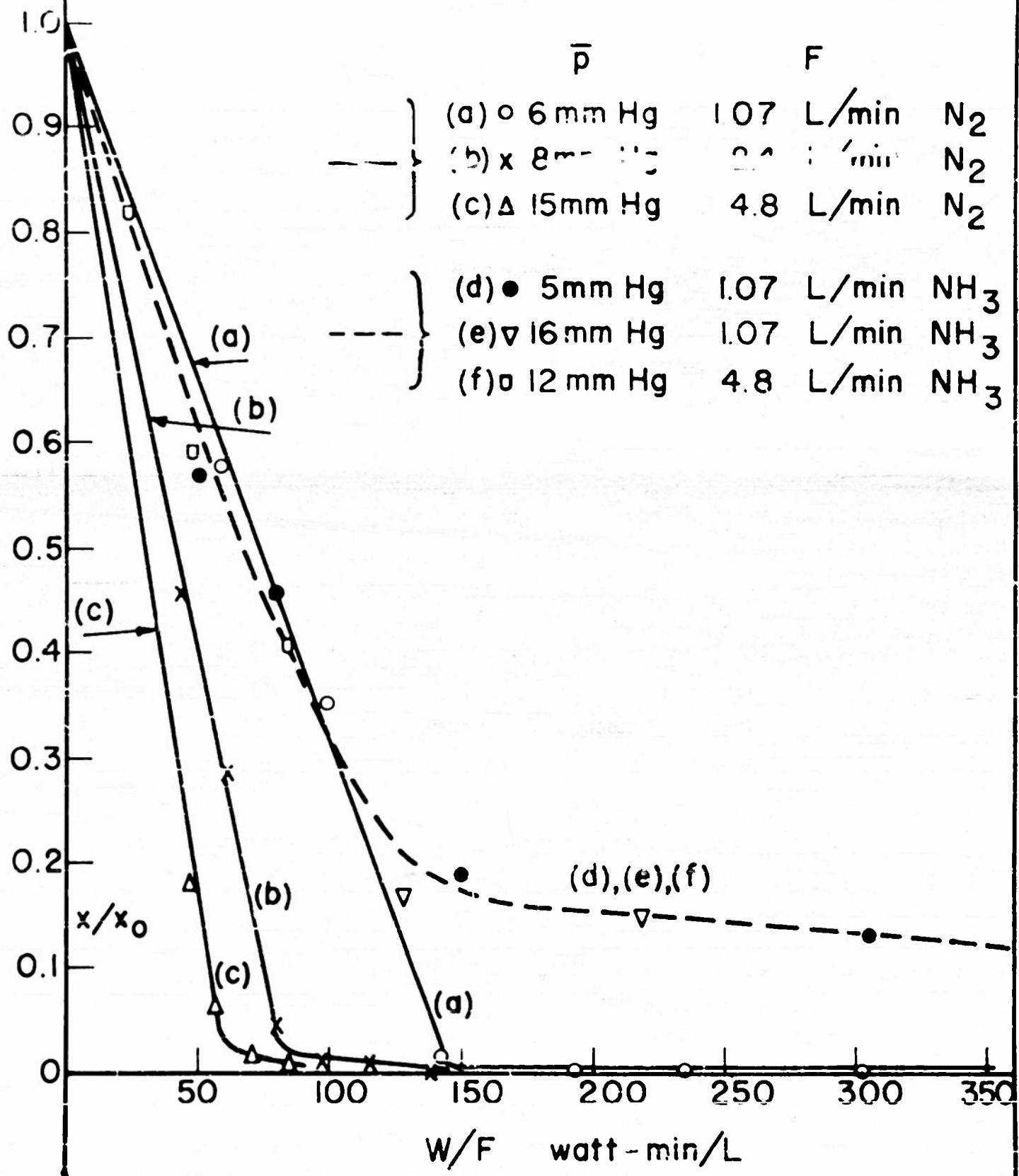
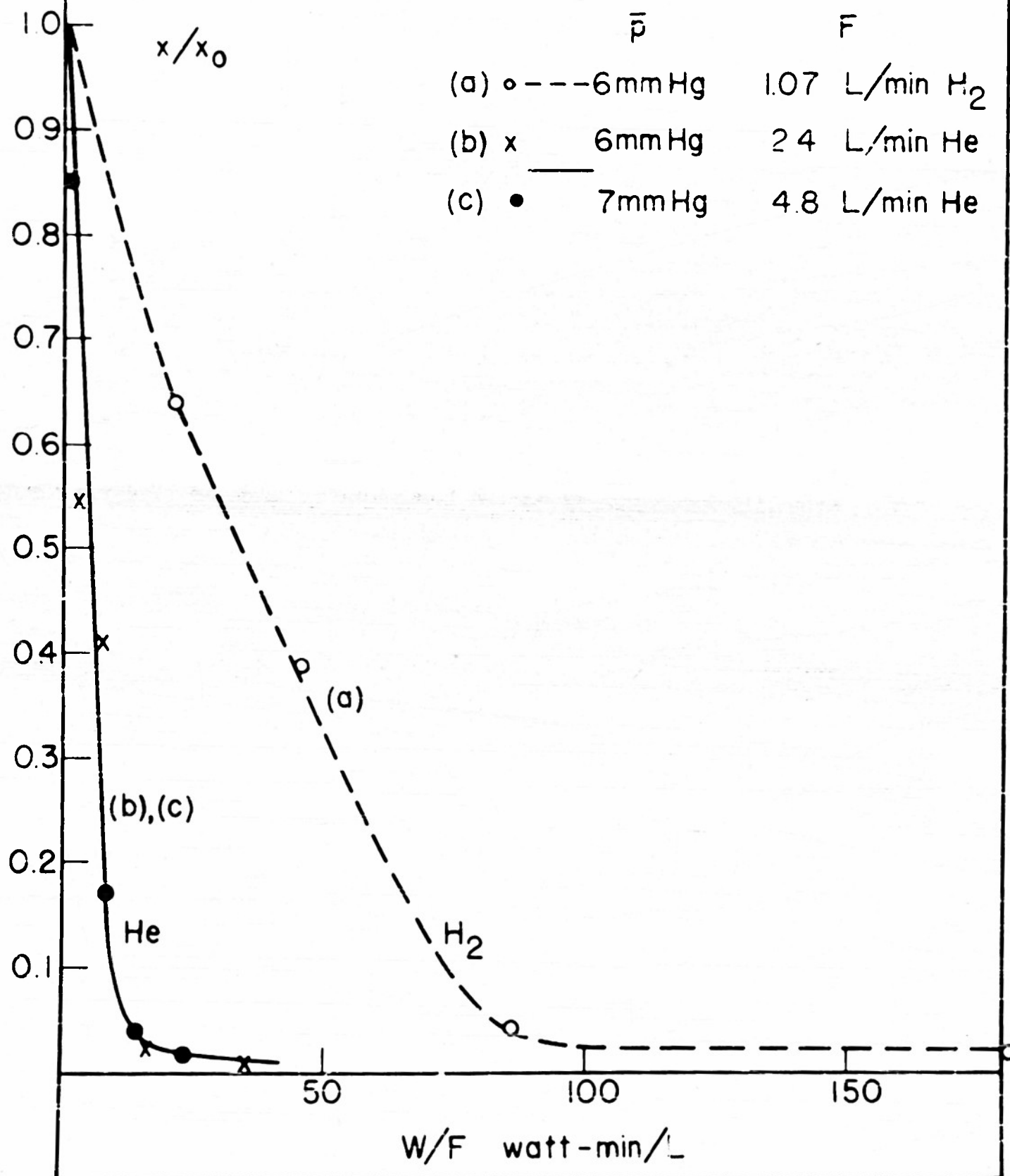


FIG. 12: DECOMPOSITION OF HYDRAZINE USING
HYDROGEN OR HELIUM AS CARRIER GASES



Here X and X_0 represent the mole fractions of hydrazine present in the carrier gas after and before passage through the discharge; W/F is the energy supplied to the mixture per unit gas volume introduced to the reactor. Inspection of the figures shows the following; (a) At a constant mass flow the fraction of hydrazine remaining after passage through the discharge decreases almost linearly with increasing power input. (b) When noncondensable gases are used as carriers this relation is obeyed down to values of X/X_0 near 0.03. Near this fractional value the slope of the curves changes abruptly and becomes nearly horizontal, indicating that further decomposition of hydrazine can be achieved only at very much increased power levels. When ammonia is used as carrier gas, the abrupt change in slope occurs near the value $X/X_0 \approx 0.2$ and the curve seems to approach the value $X/X_0 = 0.1$ asymptotically for large W/F . The difference in behavior between ammonia and the other carrier gases is due to the regeneration of some of the hydrazine by decomposition of ammonia in the discharge. In this process noncondensable gases are also formed, so that gases other than ammonia act as carriers as well. (c) As the flow rate is decreased the fraction of hydrazine destroyed at a given power level increases. Compare for example runs 173 and 182, 174 and 183, 113 and 121, or 115 and 120 in table 9. This is to be expected since at constant pressure and temperature the residence time of hydrazine varies inversely with the flow rate. (d) The fraction of hydrazine destroyed at a given power level increases in ammonia, nitrogen, hydrogen, and helium in that order.

C. Decomposition Products

The last two columns of table 9A give some information concerning the nature of the decomposition products of hydrazine in a discharge. As is shown below, these data are inconsistent with any reaction scheme involving decomposition of hydrazine into nitrogen and hydrogen only. This constitutes indirect evidence that the decomposition of hydrazine into ammonia may occur.

The effect is illustrated by experiment 119, table 9A, which is selected for the low power level at which hydrazine synthesis is known to be favorable.

Let n_1 , n_2 , and n_3 represent respectively the number of moles per unit volume, of hydrazine, noncondensable gases, and of ammonia present in the product mixture after ammonia - hydrazine mixtures are passed through the discharge. Let n_{10} and n_{30} be corresponding quantities in the starting mixture; n_{20} has the value zero. Let $n = n_1 + n_2 + n_3$ and $n_0 = n_{10} + n_{30}$.

The difference $\Delta x_1 = x_1 - x_{10}$ is given in columns 6 and 7 of table 9A. It has the numerical value $\Delta x_1 = (21.2 - 12.1) \times 10^{-3}$, i.e.

$$\Delta x_1 = \frac{n_1}{n} - \frac{n_{10}}{n_0} \approx 9.1 \times 10^{-3} \quad (16)$$

Under the conditions of the experiment $n_{10} \ll n_{30}$ and $n_1 \ll n_2 \ll n_3$; moreover, $n_1 \ll n_{10}$. In view of these inequalities it is permissible as a first approximation to set $n = n_0$.

Assume now that hydrazine is decomposed into the elements according to the equation



One then finds that

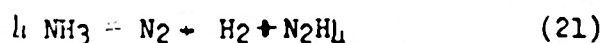
$$n_1 - n_{10} = \frac{1}{3} (n_2 - n_{20}) = \frac{1}{3} n_2 \quad (18)$$

and accordingly

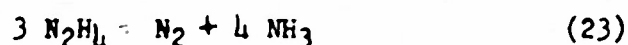
$$\Delta x_2 = \frac{n_2}{n} = \frac{3(n_1 - n_{10})}{n} \approx 3 \left(\frac{n_1}{n} - \frac{n_{10}}{n_0} \right) = 3 \Delta x_1 = 27.3 \times 10^{-3} \quad (19)$$

The experimentally observed value, taken from the last two columns of table 9A, is given by $\Delta x_2 = (32 - 16 \pm 2) 10^{-3} = (16 \pm 2) 10^{-3}$. Since this latter value is less than that computed on the basis of equation (17) it must be concluded that the decomposition of hydrazine solely into the elements nitrogen and hydrogen does not occur.

In this connection it is of interest to note that a determination of the hydrogen to nitrogen ratio in the discharge product may not give any information concerning the mechanism of the hydrazine decomposition. For example, the decomposition of ammonia might proceed according to either of the two schemes



while the hydrazine decomposition might be expected a priori to occur according to the schemes



If now equation (20) or (21) is combined with either (22) or (23) by eliminating the quantity N_2H_4 one obtains a net reaction in which the molar quantities of N_2 to H_2 are in the ratio 1 : 3.

5. DISCUSSION

A. Absolute vs. Relative Conversion

It was shown in section 3 that the use of hydrogen or helium as a diluent greatly increased the fractional conversion of ammonia into hydrazine. It must be emphasized, however, that the absolute quantities of hydrazine obtained in the presence of the diluents are no greater than those obtained in their absence. Table 10 may be used for comparison purposes. The next to last column lists the maximum relative conversion z_m under a variety of conditions. The last column lists the maximum absolute quantity of hydrazine which was obtained in the five liter volume of flask "A" under those same conditions. These numerical values were computed according to the formula $g_m = g'_m \bar{p}/p_s$, where g'_m is the maximal weight of hydrazine assayed in the flask under a given set of conditions at the sample pressure p_s , and where \bar{p} is the average gas pressure in the reactor.

Inspection of table 10 shows that while the maximal z values increase upon addition of diluent, the quantity g_m does not change significantly, under comparable reactor pressures and flow rates. Numerically, g_m has values in the range 0.1 to 0.6 mg hydrazine in a five liter volume at reactor pressures in the range 4 to 40 mm Hg. Clearly, even under optimal conditions the amount of hydrazine produced in these experiments is very low.

The principal advantage accruing from the use of inert diluents is the increase in power yield over that of pure ammonia, as is indicated in table 8.

Table 10. Comparison of Relative and Absolute Quantities of Hydrazine Produced by the Decomposition of Ammonia; F , flow rate; \bar{p} average pressure in the discharge tube; \bar{x}_0 , average mole fraction of diluent initially present; z_m , maximum value of fraction of ammonia decomposed into hydrazine on a molar basis; g_m , maximum weight of hydrazine observed in the five liter bulb "A" at the pressure \bar{p} .

Diluent	F l/min	\bar{p} mm Hg	\bar{x}_0	$z_m \times 10^3$	g_m mg
H ₂	2.1	4	.50	11.5	0.08
He	2.1	8	.39	15.5	0.26
	1.1	6	.38	17	0.21
	1.1	31	.37	5	0.34
None	2.4	5-7	0	6	0.15
	2.4	13-15	0	6	0.33
	2.4	23	0	5	0.42
	2.4	31	0	4	0.57
None	1.07	10	0	7.0	0.31
	1.07	20	0	5.0	0.32
	1.07	30	0	2.2	0.35
	1.07	40	0	2.1	0.27

B. Synthesis and Decomposition of Hydrazine in the Discharge

The decomposition of hydrazine in an electric discharge occurs very readily, as is indicated by the data of section 4. This fact places an upper limit on the hydrazine concentration which can be reached by the action of a steady electric discharge on ammonia.

A very simple method of minimizing the decomposition of newly formed hydrazine would seem to be the use of pulse discharges. The intensity and duration of the pulse should be such as to allow formation of the maximal number of free radicals or ions. These should be given a chance to undergo various recombination reactions, and any hydrazine formed should be swept out from the reactor before application of the next pulse.

6. SUMMARY

The decomposition of ammonia into hydrazine, nitrogen and hydrogen under the action of an electric discharge has been investigated, and the decomposition of hydrazine in the discharge was studied.

A water cooled Pyrex glass tube, 0.8 cm diameter, 15 cm in length, served as the reactor. The longitudinal discharge was maintained between two copper electrodes. Ammonia or noncondensable gases were introduced to the reactor through reducing valves and flowmeters. Hydrazine or water vapor could be introduced through capillary leaks if desired. After passing through the discharge tube a portion of the effluent gas mixture was led to an analytical vacuum manifold, which had been previously

evacuated to pressures less than 1 μ . Upon measuring the gas pressure in the analytical manifold, a five-liter glass bulb was removed to the analytical laboratory for hydrazine assay. Another two-liter bulb was isolated from the analytical manifold and its cold finger immersed in liquid nitrogen to freeze out condensable gases. After a lapse of 30 minutes the pressure of the noncondensable gases was determined. When diluents were employed in this work a blank sample was also obtained in the absence of the discharge to ascertain the composition of the starting mixture.

The hydrazine assay was carried out by absorbing the gas in 0.1 N hydrochloric acid, diluting aliquot portions, and developing color with p-dimethylamino-benzaldehyde. The light absorption was read on an electrophotometer.

The decomposition of pure ammonia into hydrogen and nitrogen can be characterized by the empirical equation

$$x_{nc} = 7.4 \times 10^{-4} W / \sqrt{F} - 0.028$$

where x_{nc} is the mole fraction of noncondensable gases in the effluent mixture, W the power input in watts, and F the flow rate in l/min. This equation is obeyed over power inputs ranging from 50 to 675 watts and over flow rates ranging from 1 to 10 l/min. The decomposition of ammonia into its elements is found to be independent of reactor pressure in the range 3 to 50 mm Hg.

Results concerning the decomposition of pure ammonia into hydrazine showed somewhat erratic scattering. It was found that the mole fraction

of hydrazine, $x_{N_2H_4}$, obtained in the product mixture did not depend markedly on pressure or on the ratio W/F in the range $0 < W/F < 160$. In this region all $x_{N_2H_4}$ values were observed experimentally to fall in the range 1.5×10^{-3} to 3.8×10^{-3} . The average $x_{N_2H_4}$ value obtained at a given flow rate increased slightly with decreasing flow rate. For values of $W/F > 160$ the quantity $x_{N_2H_4}$ decreased rapidly. Power yields ranged from 0.04 to 8 g. hydrazine per KWH, the most favorable yields being obtained at the lowest possible power inputs. The conversions obtained were in the range 0.4 to 0.8 g hydrazine per 100 g ammonia. For the majority of experimental conditions the ratio of moles of noncondensable gases to hydrazine produced in the discharge was in the range 200-300.

When nitrogen was used as diluent in 50-50 mixtures, the decomposition of ammonia into its elements was decreased by a factor of two, and the decomposition into hydrazine was not affected appreciably. Small quantities of water vapor were found to lower the hydrazine yield by a factor of two. Using hydrogen, the ammonia decomposition into the elements was suppressed but the formation of hydrazine was greatly enhanced. The fraction of ammonia in the starting mixture converted to hydrazine, z , passed through a sharp maximum as the power input was raised. Under optimum conditions z values in the range of .7 to 1.2 mole percent were found, corresponding to a maximum conversion of 1.2 g hydrazine per 100 g of ammonia. Power yields in this set of experiments were in the range 2.1 to 13 g/KWH. Use of helium in 40:60 ratios enhanced decomposition of ammonia both into the elements and into hydrazine. Again the quantity z was found to pass through a sharp maximum as the power input was raised. Fractional conversions

up to $x = 1.7$ mole percent were reached, corresponding to conversions of 3.4 g hydrazine per 100 g. ammonia introduced into the reactor. Depending on operating conditions, power yields ranging between 0.7 and 22 g/KWH were observed, with highest values being found at the lowest possible power inputs and at flow rates in the range 2.1 to 3.4 l/min. Thus the use of hydrogen or helium as a diluent seems to be favorable to the formation of hydrazine.

The decomposition of hydrazine in the discharge was also investigated, using ammonia, hydrogen, nitrogen and helium as carrier gas. With initial hydrazine concentrations in the range up to 4 mole percent, decomposition was found to occur readily in the discharge, the extent of which increased roughly linearly with power input. After the hydrazine concentration reached a value ranging from one to three tenths of the initial concentration, the rate of further decomposition with increasing power input levelled off. Indirect evidence is presented to show that ammonia is formed in the course of the decomposition of hydrazine.

The experimental results are discussed briefly. It is emphasized that even under condition where the relative conversion of ammonia into hydrazine is large the absolute amounts of hydrazine produced are small, i.e. of the order of 0.1 to 0.6 milligrams in a five liter volume at pressures in the range 4 to 40 mm Hg. It is suggested that hydrazine yields might be improved by use of a pulse discharge.

SOLID PRODUCTS OF THE REACTION
BETWEEN TITANIUM TETRACHLORIDE AND
HYDROGEN IN AN ELECTRIC GLOW DISCHARGE

by

C. Wooldridge and R. H. Condit

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
INTRODUCTION	1
APPARATUS	1
Preparation of reactant gases	1
Discharge reactors	2
Hot tube reactors	3
Treatment of reaction products	3
EXPERIMENTAL	4
Conditions during discharge runs	4
Conditions during hot tube runs	4
Sources of impurities	5
ANALYTICAL RESULTS	5
General remarks	5
Methods	6
Samples	7
Sample handling	8
Notes on qualitative tests	9
Notes on analytical results	10
MISCELLANEOUS OBSERVATIONS	13
DISCUSSION	14
Interpretation of experimental results	14
Evaluation of the discharge as a method for producing titanium metal	14
SUMMARY	15
TABLES	16
FIGURES	19

ABSTRACT

A preliminary study has been made of the chemical composition of the solids formed from the reaction between titanium tetrachloride and hydrogen in an electric glow discharge. The composition of these solids was compared with that of the solids formed in the high temperature thermal reaction, and the two were found to be qualitatively similar. The use of a discharge was not found in this work to offer any advantages over that of a furnace in the decomposition reaction between titanium tetrachloride and hydrogen.

INTRODUCTION

A reaction takes place between titanium tetrachloride and hydrogen in an electric discharge with the formation of solid products which in some cases may contain titanium metal. The work reported here was designed to gain some preliminary information on the total composition of the solids. The results are discussed as they relate to the possibility of developing this reaction as a practical method for producing titanium metal.

This is a continuation of work begun under a contract with the Atomic Energy Commission, contract No. S-AEC-AT-30-1-366. Apparatus constructed in the concluding months of that contract was used in these experiments. Some of the work performed under the original contract is also reviewed here.

The method of this investigation has been to analyse the solids formed in the discharge under various conditions and to compare them with the solids formed thermally in a heated tube.

APPARATUS

An outline diagram of the apparatus will be found in Fig. 1. It was built to allow easy dismantling, cleaning, and reassembling. The electric power supply used has been described in the A.E.C. report.

Preparation of reactant gases: Hydrogen from a commercial cylinder was passed over a catalyst of 0.5% palladium on alumina pellets (made by Baker & Co., Inc., 113 Astor St., Newark, N.J.) which was heated in an electric furnace to 300 - 350°C. This converted any oxygen present to

water which was removed by bubbling through concentrated sulfuric acid twice, followed by passage over activated alumina. A rotameter indicated the flow rate of the purified hydrogen. It could then either be passed directly to the reactor by opening the stopcock, S-2, or first bubbled through technical grade titanium tetrachloride and then through the needle valve, S-3, into the reactor. The stopcock, S-1, allowed hydrogen to be passed into the air while S-2 and S-3 were closed. The pressure in the line from the cylinder to S-2 and S-3 was generally maintained slightly above atmospheric pressure. All lines consisted of glass tubing joined with rubber hose, the joints being painted with glyptal.

Discharge reactors: A bulb reactor used in the discharge runs from March 11 through May 2 is shown in fig. 2. It was made from a spherical liter flask by the addition of side arms and gas exit tube at the base. The electrodes were held in position by rubber stoppers in the side arms and extended into the central region of the bulb. The interelectrode distance was less than the sum of the two electrode-wall distances. Thus, when a conducting deposit formed on the walls of the bulb (it did not form in the side arms) the reactor was not short circuited. The anode consisted of a copper disc mounted on a brass rod. The cathode was a water cooled copper probe. A pressure gauge or a mercury manometer was connected through the rubber stopper in the side arm housing the cathode. The cathode was at ground potential.

The discharge itself covered only a small volume of the bulb; hence much of the gas may have passed through the reactor without being exposed

to the discharge. To avoid this defect an axial reactor, shown in fig. 3, was built and tested on June 25. In this reactor the discharge current radiated from an axial anode to a surrounding cylindrical cathode. During a preliminary 15-minute low power run no difficulties appeared, but the reactor was tried too late for use in any of the investigations.

Hot tube reactors: Experimental runs were carried out in which the gas mixture passed through a quartz tube heated in an electric furnace. The system for the preparation of reactant gases and for the treatment of reaction products was the same as for the discharge runs. The quartz tube and furnace were mounted vertically. The gas entrance tube was admitted through a rubber stopper in the top. The connection to the sample flask at the bottom was the same as in a discharge run. The quartz tube was 2.4 cm. in diameter. The furnace was a foot long. The temperature was measured with a thermocouple in a quartz jacket down the center of the hot tube.

Treatment of reaction products: Details of the sampling procedure are given below in the section on analytical results. Two sampling flasks were generally employed in series, one directly under the reactor and connected to it by a 1 in. diameter tube and a second in which glass wool filtered out some of the smoke particles carried by the gas stream. A cold trap was generally used to protect the vacuum pump. In some cases the gases were bubbled through water to remove hydrogen chloride, unreacted titanium tetrachloride, and solids still carried in the gas stream.

EXPERIMENTAL

In the system for the preparation of reactant gases the titanium tetrachloride reservoir was always held at room temperature except for the May 1-2 run. With this one exception the molar ratio of the tetrachloride to hydrogen under equilibrium conditions would be 0.016, since the pressure of the hydrogen was one atmosphere. However, since the hydrogen was undoubtedly not saturated in passing through the liquid tetrachloride, the actual ratio must have been much lower.

Conditions during discharge runs: Details concerning experimental conditions in runs from March 11 to June 10 will be found in table I. In these runs the hydrogen flow rate was 0.6-0.1 liters per minute. The temperature of the bulb reactor was not over 70°C. in the low pressure runs and was about 150°C. in the high pressure runs.

Flow conditions were established for several minutes before the discharge was turned on. At the end of a run, after the discharge and the titanium tetrachloride flow has been turned off, hydrogen was passed through reactor for several minutes at a pressure equal to or lower than that during the run. The system was then filled with helium and the samples obtained as described in the section on analytical results.

Conditions during hot tube runs: Details of experimental conditions in the thermal reactions of the hot tube runs will be found in table II. In the April 28 run the gas mixture was passed through while the tube was

being heated up. In the other runs, the mixture was admitted after the tube has reached the final run temperature of 1100°C.

Sources of impurities: The hydrogen was not checked for impurities during the course of this work or during the A.E.C. contract. The impurities in the titanium tetrachloride also were not determined or identified.

The weight of oxygen which could have entered the system through leaks in the vacuum line is given in table IV for the runs. In no case was nitrogen found in the solid product. A run was made on April 7 in which helium saturated with titanium tetrachloride was passed through the discharge. Although no hydrogen was present, a very small, yellow-green film formed on the bulb walls and on the glass wool filter, and it may have been due to air leak.

In other runs the total weight of solid product was probably less than a gram. Only part of this was recovered as samples.

ANALYTICAL RESULTS

General Remarks: Analytical work has been directed toward identification and quantitative determination of all reaction products obtained when hydrogen and titanium tetrachloride were passed through an electric discharge. Attempts were made to analyze for titanium chlorides, the metal, its hydride, and all adsorbed gases.

The samples produced in the discharge reacted violently on exposure to air. Consequently, it was necessary to effect all transfers of samples with air excluded. No suitable equipment for routine transfers was available during the course of this work. The use of improvised equipment often resulted in loss of samples due to accidental contamination.

A second difficulty was encountered in the assay for titanium metal and also for the oxygen content of the sample. No chemical method for assay of titanium metal is available. The glass marking test, to be described later, or X-ray analysis, can be used for identification purposes. In the absence of suitable equipment for routine transfer of samples, it was not found possible to prepare specimens for X-ray analysis, despite the many attempts to do so. Equipment for oxygen determination in the many possible oxides and oxychlorides of titanium was not available. For this reason, no assays for titanium metal or oxygen are presented in this report. All titanium analyses given below refer to total titanium present in all valence states.

Methods: Titanium was determined in all samples by solution in pyrosulfate (fusion), or in heated sulfuric acid containing ammonium sulfate. This was followed by precipitation with cupferron. After precipitation, the voluminous cupferrate was collected on a filter and ignited to titanium dioxide for weighing.

Total chlorides were determined by boiling with sodium carbonate, precipitating with silver nitrate and weighing as silver chloride. To protect the lower chlorides from atmospheric contamination they had been dissolved in ethanol prior to analysis. Attempts to separate all of the chlorides of lower valency were unsuccessful.

Those compounds in the sample which volatilized below 500° were separated by means of a gas train, using helium as carrier gas. The sample, protected from air, was placed in a quartz tube and gradually heated in a furnace. In this process volatile titanium chlorides, hydrogen chloride, and hydrogen were liberated and trapped in suitable collecting devices. The remaining part of the sample was found to be stable in air and quantitative assays for chlorine and titanium (in all combining states) were obtained.

Samples: The solid material obtained from the reactor was in the form of a fine powder occasionally containing small amounts of larger crystals. Color varied from reddish purple to dull black. Contact with small amounts of air always produced rapid decomposition as could be seen in the color change to white with evolution of fumes. Samples kept under helium generally deteriorated slowly after standing two or three days. Many samples were lost through failure to perform the analyses before decomposition set in, and others were lost accidentally while trying to effect transfer under a helium blanket from the sample vessel to the analytical apparatus. In such cases, the oxidation process itself produced sufficient heat to induce oxidation of the metal and

of titanium hydride, both normally stable in air. Analysis of an exposed sample showed 65% titanium and a trace of chlorine. The material, whitish in appearance, resembled the dioxide.

The small reactor used for the electric discharge produced only small amounts of material which could be collected in sample flasks. As a consequence, duplicate analyses for checking of methods could not be carried out.

The samples were collected in several filtration flasks. One of these was situated directly below the reactor and was connected to the latter by means of a rubber tube which could be pinched off. The sidearm of the flask was connected to a smaller filtration flask using a rubber tube which could also be pinched off. The second flask contained a glass wool filter to trap small particles carried through the two receiving flasks along the gas stream.

Sample handling: The samples were transferred from these receivers while maintaining the apparatus under a blanket of helium. Alternatively, various liquids were used as a protective covering: carbon tetrachloride, water, weak acid, or ethanol. Of these, ethanol proved most effective in preventing sample decomposition. The liquid suspension could be used directly in the determination of lower chlorides (oxidizable) by titration in runs J and K. In other runs the suspension was first dried and all tests and assays performed on solid residues which consisted of titanium, chlorides along with some oxygen.

In any future work these sample handling difficulties might possibly be circumvented by the use of smaller, tared vessels connected directly onto the vacuum line of the reactor at points immediately following the discharge tube. These could then be used as an integral part of the analytical scheme without further transfer. Suitable dry boxes of the conventional type which permit of successive rapid evacuations followed by flushings with an inert gas might also be used.

Notes on qualitative tests: The test widely used in industry for the presence of titanium metal consists of the formation of a grey mark when particles are drawn with the finger over a moistened glass surface. If the metal is present the surface appears to be marked with grey lines and scratches may or may not appear. Under a microscope, small particles of the metal are found to adhere to the glass. Jagged recesses similar to those left by an abrasive or a diamond point are not found. Using this rather limited test, traces of titanium metal were detected in runs D, E, I, J, and K.

Trivalent titanium may be detected in many ways. The test found most convenient for use in this work consisted in boiling an aqueous solution of sodium acetate with the sample. A blue coloration develops if titanium is present in the trivalent state. Titrations with an oxidant are not specific for trivalence but include all oxidizable valence less than four. In titrations with 0.1N potassium dichromate the end point may be clearly seen without the use of an indicator.

Tests for the hydride were not performed because considerable quantities of sample are required for this purpose. Assays for hydrogen were carried out repeatedly and showed that the element was present in very small amounts. The quantity of discharge products obtained from the reactor was always low. Consequently, the precision of the hydrogen assays, which normally require considerable quantities of sample, was necessarily limited.

Notes on analytical results: The composition of compounds volatile up to 500°C. has been ascertained for samples D1 and E2; results are shown in Table V. These samples had been protected in helium and were placed in the quartz tube of the gas train. Helium was used in this apparatus to sweep over the reactor products and remove those substances which volatilized as the temperature of the quartz tube was raised. A water scrubbing tower absorbed hydrogen chloride and volatile titanium chlorides (di-, tri-, and tetra-). Hydrogen gas, obtained either by desorption or by decomposition of the metal hydride, passed through the scrubber, was dried, and converted to water in a copper oxide tube heated to 300°C. The water was collected in a small phosphorus pentoxide U tube for weighing. Almost all the hydrogen present in titanium hydride (limiting formula TiH_2) is liberated between 250 and 450°C.

Separate assays were performed for the hydrogen chloride, titanium, and chlorine trapped in the scrubbing tower. The non-volatile residue left in the quartz tube was analyzed for titanium only since all chlorine had volatilized.

In different runs the assays for titanium and chlorine were not very reproducible. In part, this may have been due to the presence of unreacted titanium tetrachloride which was adsorbed on the surface of the solid particles.

It was not possible to conclusively correlate the optimum titanium assays with particular conditions under which the discharge was operated.

Table VI lists results found in analysis of samples protected from air with a covering of water. In these, all titanium chlorides were hydrolyzed but any metal or hydride present remained unaffected. The formation of hydrolytic materials would increase the percentage of material of unknown composition present in the sample, since no analyses for oxygen were carried out. Thus the titanium and chloride assays were decreased. However, as a first approximation, the percentage of materials of unknown composition could be correlated with the quantity of titanium chlorides originally present in the sample. This requires the postulate that the portion of the sample which was of unknown composition resulted entirely from the hydrolysis of titanium chlorides.

Roughly, the hydrogen assays of these aqueous samples are about ten times lower than those for runs whose products were kept under helium. Adsorbed hydrogen may have been displaced by water and the residual hydrogen may constitute the fraction bound in titanium hydride. This is only a working hypothesis and no real method for distinguishing between adsorbed and bound hydrogen has been found.

Table VII shows the analytical results of the samples obtained and kept under ethanol (95%, P.G.). Lower chlorides of titanium are readily soluble in this liquid and can be easily separated from the alcohol-insoluble compounds by means of simple filtration. Results of the assays on the performed on the insoluble residue are also given in this table. It was ascertained by qualitative tests that chlorides were absent in this residue. The titanium assays of the alcohol insoluble material were higher than others obtained during previous work, although the percent of unknown material is still quite large. Significant quantities of impurity may be present. The water content of the ethanol (5%) may have contributed to the formation of chlorine-free hydrolytic products which were collected with the residue. In this manner, oxygen may have been introduced into the residue taken for analysis.

The appearance of the material collected in the sample flask below the discharge reactor was much the same as that produced by the hot tube reactor. Runs made using thermal reaction alone produced encrustations with metallic luster inside the quartz tube walls. Chemical analysis of the thermal samples showed little variation from the usual composition found in the discharge reaction products.

The methods of analysis and of sampling employed in this work on partially reduced compounds of titanium have been entirely exploratory and in no way represent more than a series of approaches toward quantitative separation of the different valences of titanium in a mixture.

MISCELLANEOUS OBSERVATIONS

The following miscellaneous observations made during the course of this work may be of interest:

1. The solid formed in the low pressure runs was generally dark red or brown in color while that formed at the higher pressures was likely to be light red-purple. Little relationship between these color differences and the chemical constitution of the samples was found, however.

2. Smoke formed in the discharge and could be seen easily in the high pressure runs. In the low pressure runs the material captured on the glass wool filter was a dirty brown. In the runs at pressures near atmospheric the material was light red-purple.

3. Above a pressure of about 40 mm. the discharge tended to become unsteady. When it flashed or sputtered a pressure pulse could be noted on the gauge, and a large cloud of smoke formed.

4. In the run of May 1-2 the electrical characteristics as a function of composition and pressure were noted. It was found that the resistance of the gas at a given pressure increased with concentration of titanium tetrachloride until with pure tetrachloride the discharge became very unsteady. For several mixtures of the titanium tetrachloride and hydrogen the voltage-pressure curve at a given current passed through a minimum at a pressure of about 40 mm.

5. Generally, more material deposited on the anode than on the cathode.

DISCUSSION

Interpretation of experimental results: On the basis of this work it appears that the composition of the products of the reaction between titanium tetrachloride and hydrogen in the glow discharge and in the hot tube are similar chemically and appearance. Table VII shows the comparative values of two thermal and one discharge sample. In each of these samples the assay for titanium and chloride is approximately the same, with the furnace samples tending to yield slightly higher titanium assays.

Work of Bock and Moser¹ has shown that in a silent electric discharge titanium trichloride is the principal reaction product between titanium tetrachloride and hydrogen. Compared to the glow discharge the silent electric discharge is relatively free from heating effects. It would appear, therefore, that the products in the glow discharge are in part the result of thermal effects.

According to these preliminary findings the use of the electric glow discharge for the production of titanium metal or hydride does not seem advantageous.

Evaluation of the discharge as a method for producing titanium metal: It would seem that the discharge performs no important function in so far as obtaining titanium metal is concerned, and its heating effect is very inefficient as compared with direct heating in a hot tube. An atomic

¹F. Bock and I. Moser Monatsh. 33: 1407-29 (1913)

hydrogen arc might be a means for attaining high temperatures for reduction of the titanium tetrachloride to the metal. However, the one experiment done here, designed to approach such conditions, gave no indication of metal production at all. (See Table I, the run of June 10)

Another difficulty to be overcome is the separation of the metal from all other products formed in the discharge. While titanium metal was found to be present in some samples, using the glass marking test, most of the titanium present was found to be chemically combined. Lower chlorides might be separated by washing in ethanol. Any hydride present in the sample could then be decomposed by heating of the residue.

SUMMARY

A preliminary investigation of the composition of the solids produced in the reaction between titanium tetrachloride and hydrogen in a glow discharge is reported.

On the basis of this work it is concluded that the use of a glow discharge shows little promise as a means for the practical production of titanium metal.

TABLE I. Discharge Experiments between TiCl_4 and H_2

Date	Analysis Number	Pressure mm. Hg.	Current amperes	Voltage across reactor V
March 11	D	5	0.10	900
13	E	40	0.12	750
27	G	70	0.12	900
April 13	H	200	0.10	1600
15	I	350	0.20	1600
June 10*	-	760	1.4	400

*The electrodes were tungsten rods in this run. The product which was light red gave no dark residue with water, and hence no metal was formed.

TABLE II - Hot tube runs

Date	Analysis number	Pressure mm. Hg.	Temperature centigrade	Linear flow rate cm./sec.
April 28*	-	40	500	2.3
June 11	K	760	1100	1 - 400
23-24	L	760	1100	0.8

*The tube cracked as the temperature reached 500°C. A small amount of colored deposit but no metallic deposit had formed.

TABLE III - Miscellaneous discharge runs

Date	Analysis number	Pressure mm. Hg.	Current amperes	Voltage across reactor V
April 7*	-	11 - 50	0.11	1100
May 1-2**	J	10 - 200	0.08-0.30	300-1600
June 25 ***	-	6	0.10	400

*See discussion on Sources of impurities

**See discussion under Miscellaneous observations, item 4.

***See discussion on Reactors and Fig. 3.

TABLE IV - Leak rate data

Date	Leak rate on vacuum line mm. Hg. increase per hr.	Length of run in hours	Weight of oxygen* leaked during run milligrams
March 11	0.2	3.0	0.5
13	1.5	3.1	3.5
27	1.2	2.2	2.0
April 13	1.2	2.5	2.3
15	1.0	2.5	1.9
May 1 -2	1.5	about 5	6.
April 7**	1.5	0.4	0.5

*Weight calculated using volume of vacuum system as 2 liters.

**See discussion on Sources of impurities.

TABLE V - Analysis of volatile components of reaction products

Run #	Vol. Ti	Vol. Cl	HCl	H ₂	Total Ti.	Unknown
D1	5.8%	12.3%	6.5%	1.8%	76%	4%
E2	5.1	11.5	4.2	2.1	71.6	10

TABLE VI - Analysis of hydrolyzed reaction products

Run #	Total Ti	Total Cl	HCl	H ₂	Unknown
D1	66.0	8.6	1.3	.11	24
D2	78.1	1.1			21
D3	68.4	9.7	.8		22
E1	56.4	18	.8	.21	25
G3	72.4	7	.6		20
H1	54.6	28.1			17
I3	68.5	3.5	1.4	.13	25

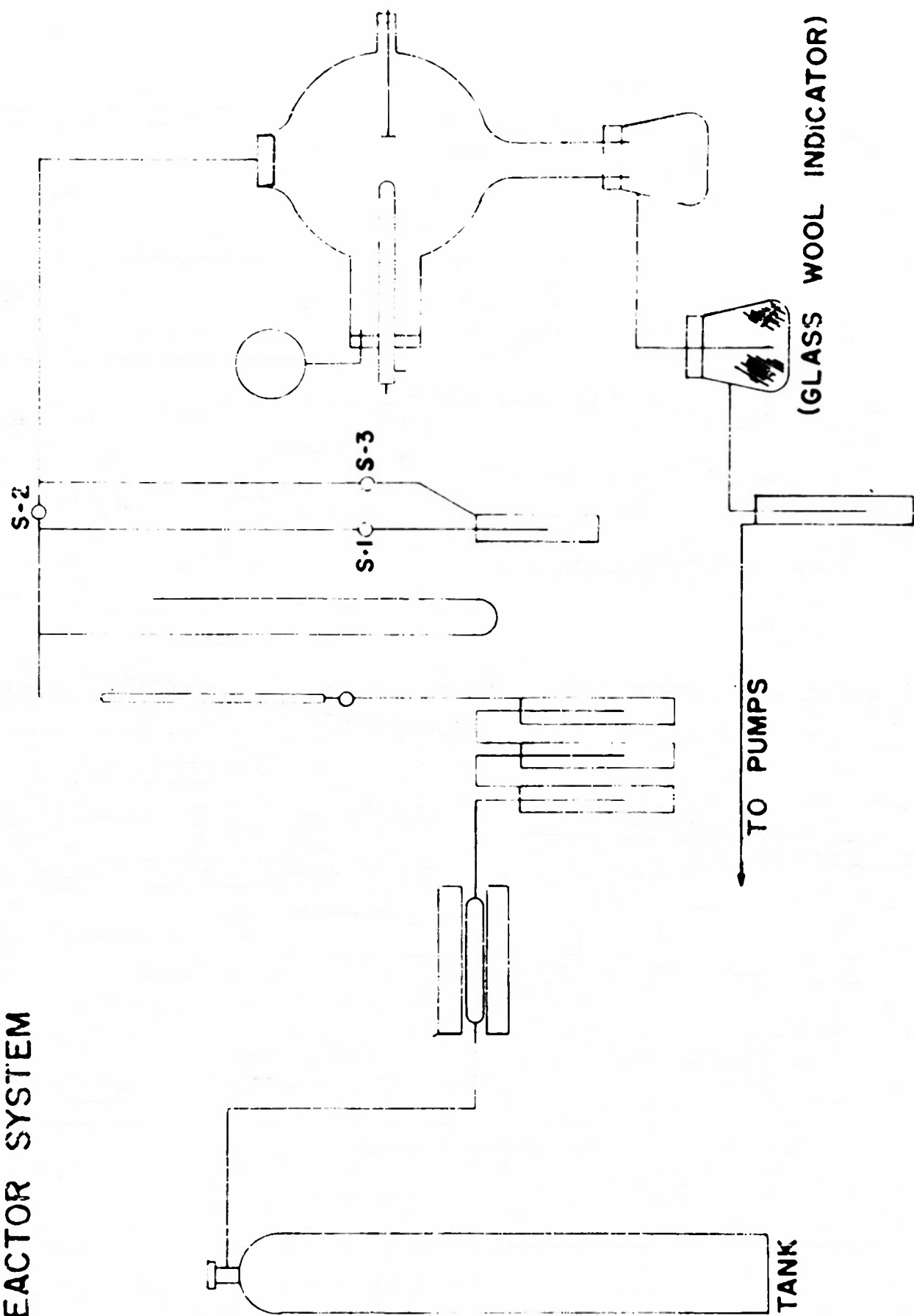
TABLE VII - Analysis of products taken in ethanol

<u>Soluble materials</u>			
<u>Run #</u>	<u>Total Ti</u>	<u>Total Cl</u>	<u>Unknown</u>
J	46.4	30.9	23
K	48.0	25	27
L	42.3	32.3	25
<u>Residue insoluble in ethanol</u>			
J	73.8	None	21
K	94.6	"	5
L	84.1	"	16

TABLE VIII - Source of samples

<u>Date</u>	<u>Run</u>	<u>Place of collection</u>
March 11	D1	From glass wool filters; under helium
	D2	Dropped from anode into water
	D3	Water rinse of reactor
March 13	E2	From flask under reactor, with helium; contained matter dropped from anode
March 13	E4	Water rinse of reactor
March 27	G3	Dropped from anode into water
April 13	H4	Material in water trap
April 15	I3	Water rinse of reactor
May 1-2	J	Bulb reactor and sampling flask;rinse with ethanol
June 11	K	Furnace sample; ethanol rinse of flask
June 23-24	L	Furnace sample; ethanol rinse of flask

FIG. 1
REACTOR SYSTEM



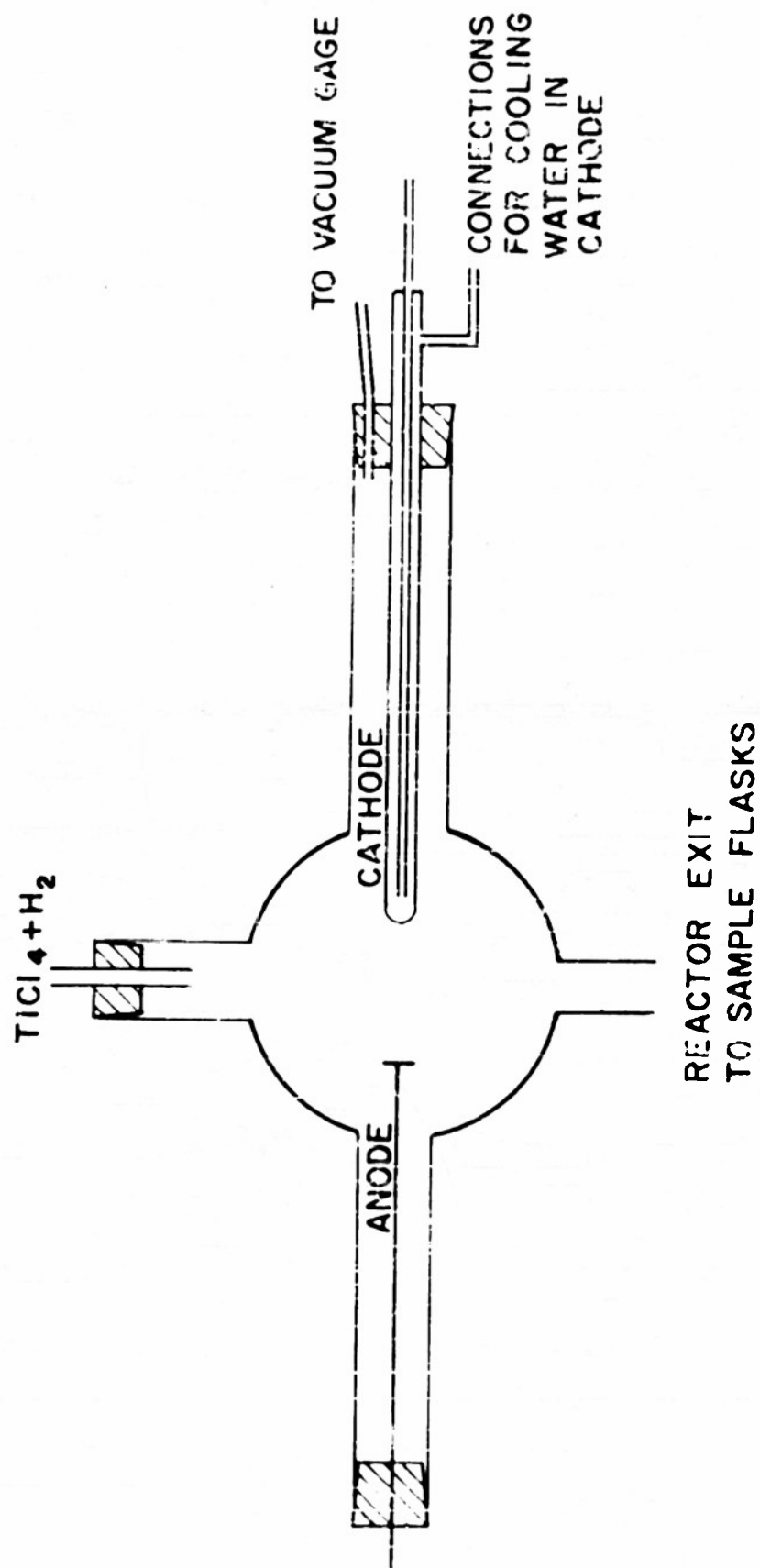


FIG. 2-- BULB REACTOR (scale 1cm.= 1in)

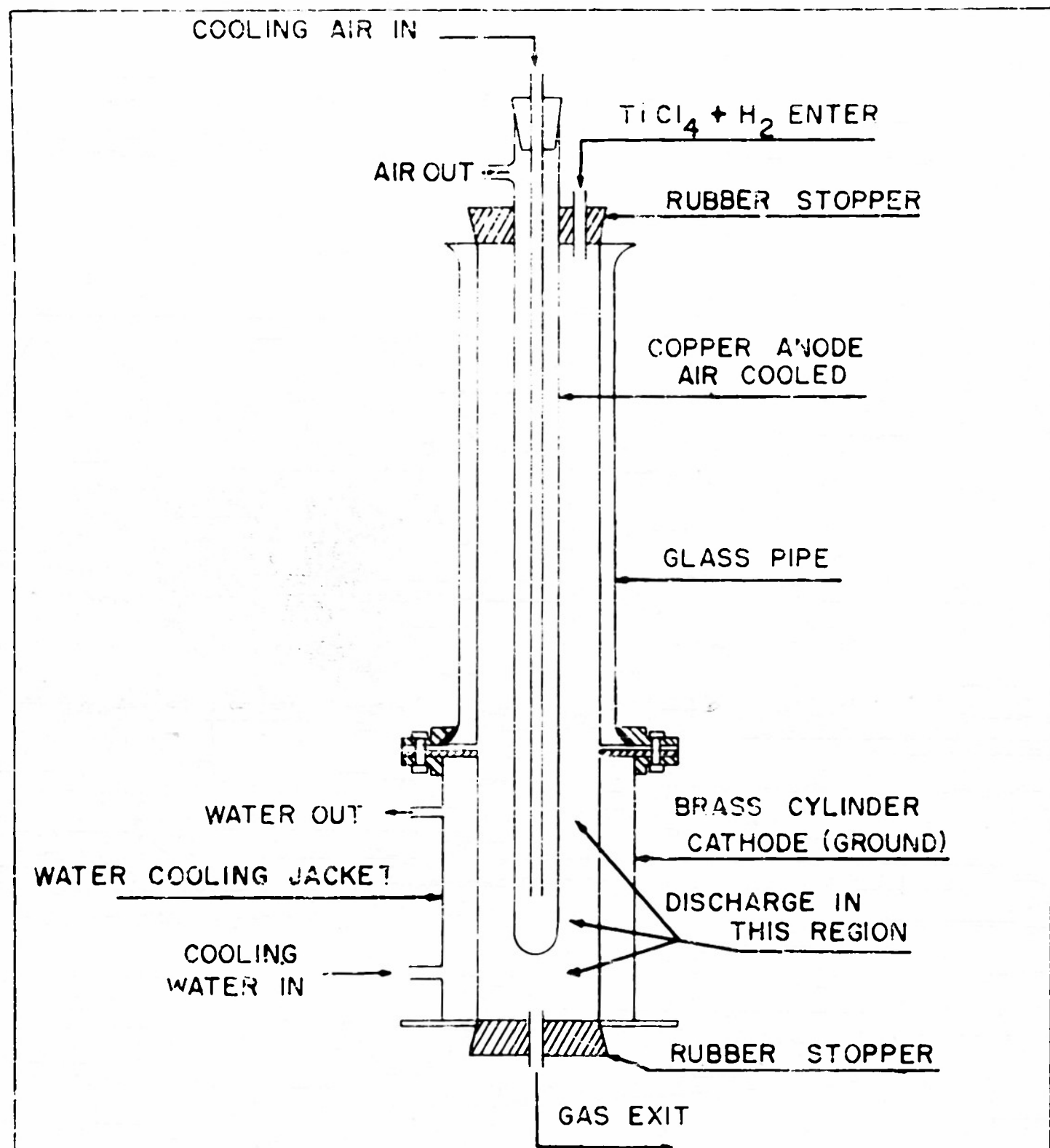


FIG. 3
AXIAL REACTOR

Distribution List

Guided Missiles Committee
Research & Development Board
The Pentagon, Room 3E613
Washington 25, D. C.

Chief of Staff, U. S. Air Force
The Pentagon
Washington 25, D. C.
Attn: DCS/M. AFMEN-4

Commanding General
Air Materiel Command
Wright-Patterson Air Force Base
Dayton, Ohio
Attn: MCIDXD
MCREXP-34

Chief of Bureau of Aeronautics
Navy Department
Washington 25, D.C.
Attn: TD-4
PP-51

Chief of Bureau of Ordnance
Navy Department
Washington 25, D.C.
Attn: Re9
Re2d

Chief of Bureau of Ships
Navy Department
Washington 25, D. C.
Attn: Code 633

Chief, Guided Missiles Branch
Technical Command
Army Chemical Center
Maryland

Director
U.S. Naval Research Laboratory
Office of Naval Research, Anacostia
Washington 25, D. C.

Commander
U. S. Naval Ordnance Test Station
Inyokern, California
P. O. China Lake, Cal.
Attn: Reports Unit

Director
National Advisory Comm.
for Aeronautics
1724 "F" Street, N.W.
Washington, D. C.

Superintendent
U. S. Naval Post Graduate School
Naval Academy
Annapolis, Maryland

Department of the Army
Office of the Chief of Ordnance
The Pentagon
Washington 25, D. C.
Attn: ORDTU

Commander
Naval Ordnance Laboratory,
White Oak
Silver Spring, Maryland
Attn: Dr. R. J. Seeger

Chief of Naval Operations
Navy Department
Washington 25, D. C.
Attn: Op-57

Director
Naval Research Laboratory
Washington 25, D. C.
Attn: Technical Information Officer

Chief, Research & Eng. Division
Office Chief of Chemical Corps
Army Chemical Center
Maryland

Distribution List

Transmitted Via

Rand Corporation
1500 - 14th Street
Santa Monica, California
Attn: R. F. Collbohm

Commanding Officer
Office of Naval Research
1030 East Green Street
Pasadena 1, Cal.

General Electric Company
Project HERMES
Schenectady, N.Y.
Attn: C.K. Bauer

Army Ordnance Liaison Officer
Building 23
G. E. Company
Schenectady, New York

Massachusetts Inst. of Technology
Project METEOR
Cambridge 39, Mass.
Attn: Guided Missiles Lab.

Development Contract Officer
Mass. Inst. of Technology
Cambridge, 39, Mass.

North American Aviation, Inc.
Aerophysics Laboratory
Los Angeles 45, Cal.

Bureau of Aeronautics
Resident Representative
Municipal Airport
Los Angeles 45, Cal.

Purdue University
Lafayette, Indiana
Attn: Dr. M. J. Zucrow

Inspector of Naval Material
410 Utility Bldg.
116 East Wayne Street
Fort Wayne, Indiana

Aerojet Engineering Corp.
Azusa, California
Attn: K. F. Mundt

Bureau of Aeronautics Rep.
15 South Raymond Avenue
Pasadena, Cal.

Director National Bur. of Standards
18 Dynamometer Laboratory
Washington 25, D. C.
Attn: Dr. E. F. Frock

Experiment Inc.
Richmond, Virginia
Attn: Dr. J. W. Mullen, II.

Development Contract Officer
P. O. Box 1-T
Richmond 2, Virginia

California Inst. of Technology
Jet Propulsion Lab.
Pasadena, Cal.

District Chief
Los Angeles Ordnance District
35 North Raymond Avenue
Pasadena 1, Cal.

Reaction Motors, Inc.
Lake Denmark
Dover, N. J.

Bureau Aeronautics Rep.
Reaction Motors, Inc.
U. S. Naval Ammunition Depot
Lake Denmark, Dover, N. J.

Distribution List

Transmitted Via

Edwal Laboratories
732 Federal Street
Chicago 5, Illinois

Commanding Officer
Office of Naval Research
844 North Rush Street
Chicago 11, Ill.

Western Cartridge Co.
East Alton, Illinois
Attn: Dr. R. L. Womer

Inspector of Naval Material
Old Custom House
815 Olive Street
St. Louis 1, Mo.

Commanding Officer
Office of Naval Research
346 Broadway
New York 13, New York

U. S. Navy Office of Naval Research
Resident Representative
c/o University of Pittsburgh
303 Thaw Hall
Pittsburgh 13, Pa.

Commanding Officer
U. S. Navy Office of Naval Research
1495 Summer Street
Boston 10, Mass.

Commanding Officer
U. S. Navy Office of Naval Research
1030 East Green Street
Pasadena 1, Cal.

Commanding Officer
U. S. Navy Office of Naval Research
601 Donahue Street
San Francisco 24, Cal.

Commanding Officer
U. S. Navy Office of Naval Research
844 North Rush Street
Chicago 11, Ill.

U. S. Navy Office of Naval Research
U. S. Navy 100
F. P. O. New York, N. Y.

Distribution List

Office of Naval Research
Navy Department
Washington 25, D. C.
Attn: Code 429

Princeton University
Princeton, New Jersey
Attn: Project SCUD
H. S. Taylor
R. N. Pease
R. J. Woodrow
D. Sayre
J. A. Farrington, Jr.